Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies

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Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies

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Table of Contents

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Abstract

Each environmental study conducted by or for the Washington State Department of Ecology must have an approved Quality Assurance (QA) Project Plan. The QA Project Plan describes the objectives of the study and the procedures to be followed to achieve those objectives. The QA Project Plan is a product of a systematic planning process.

The preparation of a QA Project Plan helps focus and guide the planning process and promotes communication among those who contribute to the study. The completed plan provides direction to those who carry out the study and forms the basis for written reports on the outcome.

This document presents detailed guidance on preparing a QA Project Plan. It describes 14 elements to be addressed in the plan and provides supporting information relevant to the content of each element.

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Introduction

Washington State Department of Ecology (Ecology) Policy 1-21 requires the preparation of a Quality Assurance (QA) Project Plan for each study that acquires new environmental measurement data or uses existing data. This document describes the content of a QA Project Plan for studies conducted by or for Ecology.

The QA Project Plan integrates the contributions of everyone involved in the study into a statement of exactly what needs to be accomplished, when and how it will be done, and by whom. It is a guide for those who implement the study as well as a basis for preparing reports on the outcome. Planners should use a "graded approach" in which the content and level of detail in a QA Project Plan depends on the type of project and the intended use of the data.

Preparing a QA Project Plan should be a team effort coordinated by the project manager. The team includes (where applicable) the client, representatives of the analytical laboratory (or laboratories), field staff, and anyone else who will contribute to the study. The team might also include specialists to provide advice on QA, information management, and statistics. A small project may not require a formal team, but rather one person interacting with people, as needed, one-on-one or in small groups.

While not usually part of the planning team, decision-makers and others with an interest in the project should be informed and consulted during planning. Once the goals of the study have been formulated, a meeting of the project team should be held to develop specific objectives for the project and to decide on the best methods to achieve them.

Field work must not begin until the plan has been approved and distributed for implementation by the appropriate personnel.

Once a QA Project Plan has been approved for a study, it may be used as a template for planning similar studies. Information specific to a new study can be inserted into the original plan. For emergency response activities, a QA Project Plan template can be prepared in advance based on available knowledge and experience, and updated as needs evolve. In this case, the plan becomes a valuable training aid for emergency response staff.

Some programs require preparation of Sampling and Analysis Plans (SAPs) that generally cover information on sampling and analysis similar to that required in a QA Project Plan. Within Ecology, the Toxics Cleanup Program requires the preparation of SAPs to comply with the Model Toxics Control Act Cleanup Regulation, Chapter 173-340 WAC. These QA Project Plan guidelines are identified by the Toxics Cleanup Program as one of the guidance documents to be used in preparing SAPs.

Preparing a QA Project Plan requires an understanding of basic concepts related to sampling, field and laboratory measurements, and assessment of data quality.

Appendices provide information, starting with a Glossary in Appendix A, to supplement the topics covered in these guidelines.

References are listed at the end of this document, followed by lists of QA requirements and guidance documents published by EPA's Quality Staff as well as additional readings on selected topics. The requirements documents provide information on satisfying the federal regulations for organizations receiving financial assistance from EPA through extramural agreements (e.g., contracts, grants, cooperative agreements, and interagency agreements). The guidance documents are intended to assist in developing and implementing a suitable Quality System, including the preparation of QA Project Plans.

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Overview of Quality Assurance and the Planning Process

In this document, Quality Assurance (QA) means a process for assuring the reliability of measurement data. QA principles and practices enable you to acquire data of the type and quality you need. The quality of the data must be documented in order to be scientifically and legally defensible.

In addition to the preparation of QA Project Plans, the following quality system components help ensure that data quality needs are met:

- Ecology's QA Policy (Executive Policy 1-21) and Quality Management Plan (Ecology, 2000)
- Manchester Environmental Laboratory QA Manual (Ecology, 2003a)
- Manchester Environmental Laboratory *Lab Users Manual* (Ecology, 2003b)
- Staff training in the principles and practices of QA
- Systematic planning
- Preparation and use of standard operating procedures (SOPs)
- Use of appropriate quality control (QC) procedures
- Verification and validation of data
- Assessment to determine whether the data support the project objectives
- Quality improvement through audits of systems and performance
- Accreditation of environmental laboratories providing data to Ecology

Ecology makes important decisions on strategies for protecting the environment and dealing with pollution. Physical, chemical, and biological data often form the basis for these decisions. QA helps ensure that data acquired by and for Ecology support correct decisions.

The potential consequences of inadequate data quality include:

- Faulty decisions
- Wasted resources
- Legal liability
- Increased risk to human health and the environment
- Inadequate understanding of the state of the environment
- Loss of credibility
- Unnecessary regulation
- Failure to regulate when necessary

Systematic Planning

Systematic planning is a process in which you identify the problem to be studied and/or the decision to be made, and then define the project's objectives, the type, quantity, and quality of information needed, the technical and QC activities, and the level of oversight that will ensure project criteria are satisfied. This information is documented in a logical sequence in the QA Project Plan.

There are two main approaches to systematic planning mentioned in these guidelines: (1) the Data Quality Objectives (DQO) Process; and (2) the Performance and Acceptance Criteria (PAC) Process. A summary explanation of systematic planning, including the DQO and PAC approaches, is given in Appendix B, and a detailed explanation of the DQO Process is provided in EPA QA/G-4.

Purpose of a QA Project Plan

The purpose of preparing a QA Project Plan is to ensure that all necessary steps are taken to acquire data of the type and quality needed.

A project or study is a logical sequence of activities grouped into three categories:

Planning $\rightarrow$ Implementation $\rightarrow$ Assessment

A QA Project Plan documents the planning phase and guides implementation and assessment.

A QA Project Plan

- Lists the goals and objectives of a study
- Identifies the type and quality of data needed
- Describes the sampling and measurement procedures needed to acquire those data
- Describes the QC and assessment procedures needed to ensure that the study objectives are met

Preparing a QA Project Plan

A systematic or step-wise planning process is essential to the successful acquisition of useful environmental data. Once you begin field work, your options are limited by what you know and what you have with you.

Ecology Policy 1-21, *Establishing Quality Assurance*, applies to environmental data collection studies/activities conducted or funded by Ecology. The policy states that a QA Project Plan "is prepared for each environmental study/activity that acquires or uses environmental measurement data."

The levels of effort and detail in preparing a QA Project Plan should be commensurate with the scope of the study and available resources. The planning process generates performance and acceptance criteria for the quality of data as well as objectives for the quality of decisions made on the basis of those data.

Preparation of a QA Project Plan serves three important functions:

- Focuses the project team on issues affecting data quality while they can still be effectively addressed (i.e., before data are acquired).
- Promotes and facilitates communication among those involved in the project.
- Compiles information needed for project implementation and assessment.

The credibility of your data may be compromised if the procedures used to acquire them are not adequately documented. The QA Project Plan provides important initial documentation of your study and identifies other necessary documentation such as:

- Standard operating procedures (SOPs)
- Field logs
- Outputs from field instruments
- Chain-of-custody records
- Lab records and reports
- Photos and drawings
- Project reports

Responsibility for Preparing QA Project Plans

Those with responsibility for QA Project Plans include:

- Ecology staff with overall responsibility for conducting a project (project managers) prepare QA Project Plans with input from their project teams.

- Ecology staff who administer grants or contracts for projects which acquire environmental data ensure that satisfactory QA Project Plans are prepared by the grantees or contractors.

- Ecology staff with oversight responsibility for projects conducted to comply with regulations or agreements ensure that satisfactory QA Project Plans are prepared by or for the responsible parties.

- Organizations funded by Ecology for environmental data collection studies and activities that acquire and use environmental measurement data are required to prepare QA Project Plans.

Responsibility for Reviewing and Approving QA Project Plans

At Ecology, QA Project Plans are generally reviewed by the project manager's supervisor, the client, laboratory QA staff (if laboratory services are required), the program QA Coordinator or agency QA Officer, and other key staff as appropriate. Allow at least two weeks for review. Some Ecology programs have standard procedures governing review and approval of QA Project Plans. Ecology staff with specialized expertise may be available to review your plan. Appendix C is a checklist to aid in the review of QA Project Plans.

The project manager makes any necessary changes to the plan based on reviewers' comments and submits the revised plan for approval signatures. Plans prepared by Ecology should be approved by all reviewers. The agency QA Officer must approve all project plans submitted to EPA.

Copies of the approved QA Project Plan are distributed to the signatories and to everyone responsible for implementing the study. QA Project Plans prepared by Ecology's Environmental Assessment Program are available as publications on Ecology's internet web site at http://www.ecy.wa.gov/biblio/eap.html.

The QA Project Plan must be approved and distributed before field work is started. Conditional approval for implementation may be given when only non-critical deficiencies remain to be resolved. The plan is then resubmitted for final approval when the information is finalized. The plan is a living document that should be updated during the course of a study whenever it is appropriate to do so.

Role of the Laboratory in a Project

The management and staff of the laboratory contribute to the success of the project by:

- Advising on selection of analytical methods that meet measurement quality objectives (MQOs)
- Advising on acceptance criteria for data drawn from existing sources (i.e., secondary sources)
- Reviewing and approving the QA Project Plan
- Providing containers and other sampling supplies (e.g., labels, forms)
- Analyzing samples using the methods selected for the project
- Carrying out appropriate QC procedures to confirm that MQOs have been met
- Reporting results for samples and QC procedures
- Documenting performance characteristics for methods used
- Providing information on how QC limits are set and how they are used for lab QC
- Reviewing data and verifying results

Elements of a QA Project Plan

The following elements comprise a complete QA Project Plan:

1. Title Page with Approvals
2. Table of Contents and Distribution List
3. Background
4. Project Description
5. Organization and Schedule
6. Quality Objectives
7. Sampling Process Design (Experimental Design)
8. Sampling Procedures
9. Measurement Procedures
10. Quality Control
11. Data Management Procedures
12. Audits and Reports
13. Data Verification and Validation
14. Data Quality (Usability) Assessment

The project manager may decide that some elements can be omitted or merged into other elements. Factors which influence these decisions include the scope and complexity of the project, the number of staff involved and their level of expertise, and past problems which could be avoided by clearly stating expectations in the plan. Criteria to help the project manager make these decisions are provided in the discussions of the individual elements that follow. If you omit an element because it is not applicable, state why it was omitted.

The level of detail in a QA Project Plan depends on the type and complexity of the project and the intended use of the data. The information in the QA Project Plan must be sufficiently detailed to allow those responsible for review, approval, and implementation of the plan to understand what is to be done and the reasons for doing so.

Documents containing information relevant to the study are referenced in, or appended to, the QA Project Plan.

Project plans prepared to meet EPA requirements must address the elements described in the most recent versions of EPA Documents QA/R-5, *EPA Requirements for Quality Assurance Project Plans*, and QA/G-5, *Guidance for Quality Assurance Project Plans***.** See Appendix D for a list of the elements included in these documents.

For hazardous waste programs, especially those that are Superfund related, you may need to follow the *Uniform Federal Policy for Quality Assurance Project Plans* prepared by the Intergovernmental Data Quality Task Force (IDQTF, 2003).

The following pages provide guidelines for the information to be included in each of the 14 elements of a QA Project Plan. Key information to be included in each element is highlighted in **bold type**.

1. Title Page with Approvals

The following information is presented on the title pages of the plan:

- **Title**
- **Author**
- **Author's organization**
- **Date the plan was prepared or revised**
- **Other information useful in identifying the study (e.g., a document, grant, geographic location, or contract identifier)**
- **Spaces for approval signatures and dates**

Plans prepared by Ecology usually include an additional cover page without the signatures. Signatures indicate both approval of the plan and commitment to support implementation of the procedures specified.

Plans prepared by Ecology should be approved by:

- The project manager
- The project manager's supervisor
- The client
- A representative of the laboratory, if a lab is involved in the project
- The program QA Coordinator or agency QA Officer
- Other key staff as appropriate

At Ecology, the agency QA Officer must approve all project plans submitted to EPA. For projects conducted under a grant or contract, the Ecology grant or contract administrator may approve the plan after comments from technical reviewers have been addressed.

2. Table of Contents and Distribution List

Include a Table of Contents.

The table should be included if it would be helpful to those using the plan, as is the case for longer plans. It directs the user to the project plan elements and to tables, figures, references, and appendices.

Those who will receive copies of the approved plan may be listed after the Table of Contents.

Provide names of individuals, along with their affiliation, address, phone number, and e-mail address.

3. Background

One of the first steps in a systematic planning process is to give an overview of why the project is needed. This element and the next describe why the project will be done and what needs to be done; these may be combined into a single element if that would improve clarity. Provide enough background information so that the reasons for conducting the study are clear. Give the reader a perspective of the present situation and the events leading up to it.

For projects in which new data are to be collected, it may be necessary to make a reconnaissance visit to gather information on conditions, accessibility, and activity in the area, before completing your plan.

Where applicable, provide the following:

Describe the study area and surroundings.

Include sufficient detail that reviewers can determine whether the study design and field procedures are appropriate. Include maps, photos, or drawings of the site or area.

Mention any logistical problems with the study area.

Note items such as limited access or the presence of hazardous substances which require unusual procedures.

Relate the history of the study area.

Use drawings or photographs to support the narrative.

Identify parameters or contaminants of concern, and state why they are of concern.

Include information on the sources, forms, quantities, and fates of known or suspected contaminants.

Summarize the results and conclusions of previous studies.

Provide all information relevant to the study being planned. This should include existing data, using tables and charts if necessary. State how these data are relevant to the objectives of your new study. Reference the reports that are the sources of these data.

Identify important related criteria or standards.

4. Project Description

From the information in Element 3 and outputs from your systematic planning process, provide the following:

State your goals.

The goals are your reasons for conducting the project.

Describe the nature of the problems that will be studied, the questions to be answered, the decisions to be made, and the actions that might result from the decisions.

State your objectives.

The objectives are what you want to accomplish.

It is essential to document your overall project objectives because they form the basis for the rest of the plan. Clear objectives preclude unrealistic expectations and facilitate planning and communication. More specific objectives for the quality of the decisions and measurements will be included in Element 6.

Identify the information, including data, needed to meet your objectives.

Provide just a summary here. Details will be covered in the subsequent elements of the plan. Indicate which information is already available from previous studies and which will require new environmental measurements. Identify which parameters or contaminants of concern need to be identified and measured.

Identify the target population.

The target population might be one of the strata in a lake in the springtime, contaminated soil at an abandoned industrial facility, or tissue from the shellfish in a particular estuary. The population is characterized by its boundaries in time and space as well as its relationship to its surroundings.

Define the study boundaries.

This will help ensure that data will be representative of that population. Use existing information and professional judgment to stratify or segregate the population into categories with homogenous characteristics.

Identify any practical constraints on the study design.

Include items such as seasonal or meteorological conditions, limited access, or availability of personnel or equipment.

Summarize the tasks that will be required to collect the data.

Describe any decisions that will be made using the project data.

An objective of some environmental studies is to acquire data for comparison to specific regulatory criteria or to existing data. The comparison then forms the basis for a decision on whether some action is required. Decisions are rarely made on the basis of a single result. Appendix E provides a discussion of the effects of errors on decisions. Decision quality is addressed in Element 6, *Quality Objectives.*

5. Organization and Schedule

Identify members of the project planning team, decision-makers, and interested parties.

Study participants need a clear understanding of their roles and their relationship to the overall effort. A planning team meeting is recommended to discuss individual roles and responsibilities and the schedule for implementing the plan. For a small project, it may be sufficient to have one person interacting with others, as needed, one-on-one or in small groups, rather than in formal meetings.

Identify everyone involved in implementing the study and assessing the data.

Include names, organizations, phone numbers, and responsibilities of key personnel.

For large studies, include an organization chart showing the lines of communication among participants.

Include a schedule for the project.

Provide proposed dates for

- Reconnaissance visits
- Preparation and approval of the QA Project Plan
- Field activities
- Delivery of samples to the laboratory
- Reporting measurement results
- Verification and validation of data
- Data entry to Ecology's Environmental Information Management System (EIM) or other database
- Progress, draft, and final reports, as needed
- Disposal of samples

The final preparation of the schedule may be one of the last steps in the preparing the project plan.

Describe limitations imposed on the schedule.

Discuss factors such as weather, seasonal conditions, equipment availability, etc. Plan to keep the laboratory informed of your schedule for delivery of samples.

Plan to obtain all necessary collection permits and permissions to access property and take samples before scheduling reconnaissance visits or field activities.

Include budget information for the project, if required.

6. Quality Objectives

There are several factors that affect the quality and usefulness of data, and therefore impact the decisions made on the basis of those data. The overall quality of your data will be determined by a combination of those factors. Data may be affected by systematic errors (i.e., bias) and are always subject to random errors. It is often necessary to report results at very low concentrations, where random error is generally large relative to concentration.

Quality objectives need to be specified at two levels when critical decisions must be made and at only one level when decision-making is not the purpose of data collection.

There are several approaches to systematic planning. Summary descriptions of these are given in Appendix B. The approach used for systematic planning will depend on whether or not decision-making is a primary purpose of data collection.

Precision, bias, and sensitivity are data quality indicators used in establishing quality objectives. Other data quality indicators are representativeness, comparability, and completeness; these are discussed in Element 7, *Sampling Process Design*.

Before reading the following guidelines for the quality objectives that need to be specified in your plan, it is recommended that you read the addendum to this element, which includes background information on the concepts of precision, bias, and sensitivity.

Decision Quality Objectives

When data will be used to select between two clear alternative conditions or to determine compliance with a standard, such as in some hazardous-waste site cleanups, quality objectives at the level of the decision are required. They specify how good a decision must be, but do not directly set criteria for the quality of the data or express data quality characteristics. The outputs of a Decision (or Data) Quality Objectives (DQO) Process are needed to determine the number of samples that must be taken and analyzed. A brief explanation of the DQO Process is provided in Appendix B, and detailed explanations are given in EPA QA/G-4, *Guidance for the Data Quality Objectives Process* and EPA QA/G-4HW, *Data Quality Objective Process for Hazardous Waste Site Investigations*. Appendix E explains the statistical basis for decision-making.

Measurement Quality Objectives

Measurement quality objectives (MQOs) specify how good the data must be in order to meet the objectives of the project. MQOs are the performance or acceptance thresholds or goals for the project's data, based primarily on the data quality indicators precision, bias, and sensitivity. Another name for MQOs is measurement performance criteria (MPC). For existing data, these correspond to acceptance criteria.

MQOs are included in all QA Project Plans.

In the DQO Process, the tolerable limits on decision errors are the basis for specifying the MQOs.

In other projects when data are being used to support estimation, modeling, or research and are not directly linked to a decision, the required accuracy of measurement results is the basis for establishing MQOs.

MQOs are used to select procedures for sampling, analysis, and quality control (QC).

A simple approach to specifying MQOs is recommended for most projects. In this approach, MQOs are expressed in the same units used for reporting QC sample results. This facilitates data validation, since the results for QC sample analyses can be compared directly to determine whether the MQOs have been met. Although the MQOs are expressed in the same units as QC sample results, they do not specify the analytical method or technology to be used.

The MQOs selected should be compatible with the requirements for accuracy (precision and bias), as defined in the addendum to this element. The following examples are stated in the same units used by the laboratory for reporting their QC results.

Examples of MQOs for a project analyzing metals in water samples are:

- Check Standards/Lab Control Samples – 85 to 115% Recovery
- Duplicate Sample Analyses – ≤ 20% Relative Percent Difference (RPD)
- Matrix Spike Recoveries – 75 to 125%
- Duplicate Matrix Spikes – ≤ 20% RPD

Examples of MQOs for a project analyzing orthophosphate and nitrate in water samples are:

- Check Standards/Lab Control Samples – 80 to 120% Recovery
- Duplicate Sample Analyses – ≤ 20% RPD
- Matrix Spike Recoveries – 75 to 125%
- Duplicate Matrix Spikes – ≤ 20% RPD

Examples of MQOs for a project analyzing organochlorine pesticides in water samples by EPA method 8081 are:

- Check Standards/Lab Control Samples – 30 to 150% Recovery
- Surrogate Compounds – 30 to 150% Recovery
- Duplicate Sample Analyses – ≤ 50% RPD
- Matrix Spike Recoveries – 30 to 150%
- Duplicate Matrix Spikes – ≤ 50% RPD

See Element 10, *Quality Control*, and Appendix G for explanations of the QC terms used above.

Some parameters, such as Biochemical Oxygen Demand (BOD), and bacteriological determinations are defined operationally by the procedures used in their determination. There are no standard solutions that can be used to check overall accuracy, although it may be possible to check precision. For those parameters, it is important to ensure that the written procedures are followed exactly, and MQOs may be limited to the precision for replicate analyses of samples and standards.

For some field measurements, such as pH, temperature, and electrical conductivity, fewer MQOs can be specified, since not as many QC checks can be done in the field as in the controlled environment of the laboratory. In those cases, it is important to operationally ensure that instruments are calibrated regularly and the calibration is checked frequently. MQOs can sometimes be expressed in terms of the maximum deviations allowed for calibration checks.

MQOs for sensitivity should be expressed as the lowest concentrations of interest. A rule of thumb used to determine the lowest concentration of interest is that it be ten times lower than the reference level used for decision-making (i.e., the standard, criterion, or regulatory limit). For example, if you are determining a substance subject to a water quality standard of 100 µg/L, the smallest concentration of interest should be specified as 10 µg/L. This helps ensure that the method selected for use will be precise enough for reliable decision-making when results are at or near the 100 µg/L water quality standard. For some parameters, such as pH, it may not be meaningful to specify a lowest concentration of interest.

Prepare a table summarizing your MQOs for both lab and field measurements.

An example of a table of MQOs is given in Appendix H.

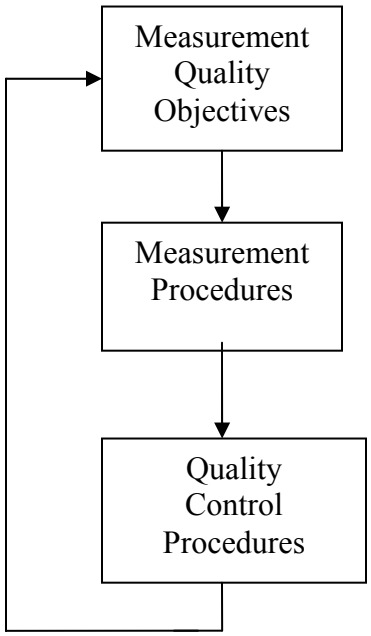
You can also specify acceptance criteria for data collected previously that will be used during the project.

MQOs also may be specified for total random error due to sampling and analysis. However, since there can be many variables affecting sampling error, it is best to set MQOs based on historical data for the parameter in a similar matrix. The most frequently stated MQO for total random error is the precision of duplicate (collocated) field samples in terms of the RPD.

An example of another way to express an MQO that includes both sampling and analysis is: "The overall precision of lead measurements taken on the soil in the bins must be less than 50% relative standard deviation when at least 10 samples are taken from each bin." This and other examples for specifying MQOs in hazardous site characterization and cleanup projects are included in an article by Crumbling (2001).

The Water Research Centre (WRC) in England has recommended a statistically based approach to analytical quality control (AQC) for water quality monitoring that (1) defines MQOs in terms of precision, bias, and lowest concentration of interest, (2) confirms that those objectives have been met prior to routine sample analysis, and (3) subsequently verifies that the objectives are met on a continuing basis. The WRC approach, summarized in Appendix F, is recommended for water quality monitoring projects if time and resources permit. This approach can be particularly useful when several laboratories are involved in a project.

As stated previously, MQOs provide the basis for choosing measurement procedures. And once measurement procedures are chosen, appropriate QC procedures are specified. This stepwise process is summarized in the following diagram.



Note that this flowchart has a feedback loop. This is to ensure that the measurement procedures and QC procedures are compatible with the MQOs. In actual practice, during the early stages of project planning, the planning team will be considering which specific methods and procedures may be applicable. It may be necessary to adjust the MQOs or the way analyses are done if methods or QC procedures are not available to meet the MQOs. For example, if the MQOs cannot be met by analyses of individual samples, it may be possible to take replicate field samples and/or do replicate analyses to obtain mean results with better precision that allows those MQOs to be met. If methods are not available to meet the initially-stated MQOs, you can evaluate whether the MQOs can be changed without compromising the overall objectives of the project. Of course, in some cases it may be necessary to develop analytical methods that will meet the MQOs before the project can proceed.

It may not be possible to meet your MQOs for precision at very low concentrations because relative error increases rapidly near the detection limit. Also, for matrix spikes, the ratio of the amount spiked to the amount present before spiking will affect the percent recoveries. These factors must be taken into account when setting MQOs and interpreting results. See Element 10, *Quality Control*, for more detail.

While emphasis has been placed on defining analytical or measurement MQOs rather than sampling MQOs, it does not imply that measurement error is always greater or more important than sampling error. For many projects, in particular the investigation and restoration of contaminated sites, sampling error rather than analytical error has been found to be the largest source of uncertainty in environmental data. When this is the case, little is gained by minimizing analytical uncertainty if sampling uncertainty is not also addressed.

One way to minimize sampling uncertainty is to collect more samples. As cost is often a concern in analyzing samples, one solution may be to use low-cost field analytical methods when available. In this way, many more samples can be analyzed to get a more accurate appraisal of contamination than is possible using conventional laboratory analyses.

The next element, Element 7, considers the importance of sampling process design in achieving MQOs.

Addendum – Background Information on Precision, Bias, and Sensitivity

Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Random errors are always present because of normal variability in the many factors that affect measurement results. Precision can also be affected by the variations of the actual concentrations in the media being sampled.

Potential sources of random errors include:

- Field sampling procedures
- Handling, transporting, and preparing samples for shipment to the laboratory
- Obtaining a subsample from the field sample for analysis
- Preparing the sample for analysis at the laboratory
- Analysis of the sample (including data handling errors)

The magnitude of these errors can be expected to vary during the measurement process and make it more difficult to determine the natural variability of contaminants in the environment.

The dispersion (width) of the familiar bell-shaped curve, or normal distribution, provides an estimate of precision. See Appendix G for a discussion of the normal distribution and equations for estimating standard deviation and other measures of precision. Note that any estimate of a population parameter can be improved by increasing the number of results used in the calculation. Historical data may offer an indication of the precision you can expect for the data you plan to acquire.

It may be more efficient to use less precise and less expensive screening techniques or measurement procedures if they can meet your MQOs. The standard error (i.e., precision) of the mean is given by $s/\sqrt{n}$, where s is the estimated standard deviation for the population of individual analytical results. Therefore, if you use the mean of n values as your result, the precision of that result is improved by a factor of $1/\sqrt{n}$ over that of an individual result (see Appendix G). Thus, a result obtained by averaging the values from several replicate measurements may be as precise as a single value obtained by a procedure with better precision.

Composite sampling (i.e., physically combining and homogenizing environmental samples or sub-samples to form a new sample) can also lower the cost of improving precision. Averaging the analytical results of a few composites can produce an estimated mean that is as precise as one based on many more individual sample results.

Bias

If a physical or chemical measurement is repeated many times using sufficiently sensitive procedures, the results will be distributed symmetrically about their mean value. Conceptually, the analyst could make an infinite number of analyses; this is termed the *population*. Bias is the difference between the population mean and the true value of the parameter being measured. Unlike random error, bias is generally not reduced by making more measurements.

Potential sources of bias include:

- Sampling procedures (including faults in sampling design)
- Instability of samples during transportation, storage, or processing
- Interference and matrix effects
- Inability to measure all forms of the parameter of interest
- Calibration of the measurement system
- Contamination of equipment, reagents, or containers

Bias due to sample collection, transportation, and storage must usually be inferred through careful observation and professional judgment. These errors can be avoided or minimized through use of standardized procedures by properly trained staff. Bias affecting measurement procedures can be inferred from the results of QC procedures involving the use of blanks, check standards, and spiked samples described in Element 10.

Generally, it is not possible to directly estimate the total bias of analytical results. Instead, each of the potential sources of bias is evaluated separately. For example, where interference or matrix effects are found, additional cleanup steps may help correct for this source of bias in some analyses.

When a measurement result is used to decide whether the true value exceeds a criterion or standard, the possibility of bias must be considered since unidentified bias can lead to an erroneous conclusion.

Keep in mind that the most effective way to deal with bias is to select sampling and measurement procedures that are not likely to introduce systematic error in the first place.

Note that if a decision will be based on the difference between two results that are equally biased, that difference may not be biased. An example might be the comparison of measurement results from the same laboratory for samples taken upstream and downstream of an outfall.

Sensitivity

For some projects, an important consideration is selection of a method capable of producing accurate results at or near the reference level(s) for decision-making (i.e., the standard, criterion, or regulatory limit). It is important that the method used for analysis

has a detection limit well below the reference level, since precision is poor near the detection limit and decisions should not be based on imprecise data.

Sensitivity in analytical chemistry reflects the ability to discern the difference between very small amounts of a substance. In general, sensitivity denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined.

However, as a data quality indicator in this document, sensitivity is also defined in a specialized sense as the lowest concentration of a substance that can be detected or the lower limit of detection described by Morrison (1965). *The MQO for sensitivity is the smallest concentration of interest for a project.* A rule of thumb is that the smallest concentration of interest be specified as one-tenth the concentration at the reference level for decision-making. The laboratory must be capable of reporting results down to that level. Element 9, *Measurement Procedures*, discusses how the MQO of smallest concentration of interest is used when choosing an appropriate analytical method.

MQOs and Accuracy

When MQOs are expressed in the same units as QC sample results, their implications for the accuracy (precision and bias) of sample results may not be apparent. It is important to understand these relationships in order to choose MQOs consistent with the fundamental accuracy requirements for your data.

For example, a check standard (lab control sample) recovery range of 85 to 115% indicates that the maximum acceptable percent relative standard deviation (%RSD) for those QC results is 5% or less, assuming that the range corresponds to action limits of ± 3 standard deviations from the mean. Because the recovery limits are symmetrical around 100%, it also indicates that calibration is not a source of bias for these analyses. The only source of bias for analyses of check standards prepared in pure water is calibration, since there should be no interference or matrix effects.

A value of 20% RPD for analytical duplicate results corresponds to approximately 14% RSD, using the equation in Appendix G.

Matrix spike recoveries that exceed QC limits may indicate the presence of bias due to interference or matrix effects, but there are many variables that can make it difficult to interpret the results of spike recoveries. In general, spike recovery results are most reliable when the ratio of the amount spiked to the concentration before spiking is approximately equal to one. When the ratio is too low, random error makes it more difficult to identify the presence of bias. When the ratio is too high, interference effects at lower concentrations may not be apparent.

7. Sampling Process Design (Experimental Design)

Prepare your design using the information developed in Elements 3, 4, and 6. It may be helpful to evaluate alternatives and select the most efficient design that will satisfy your objectives. Some regulatory programs have specific requirements for sampling design, and these should be described or referenced in this element.

Describe the sampling process design for your study.

Include:

- Samples to be collected
- Chemical, physical, and biological parameters to be determined
- Measurements to be done in the field
- Measurements to be done in the laboratory
- Locations and schedule for sampling and measurements

Provide maps or diagrams.

Show the physical boundaries of the study area as well as proposed measurement and sampling locations.

Some studies may need to include reconnaissance sampling to aid in the selection of sampling locations.

Simple conceptual models may be helpful in sampling process design. From a look at the hydrograph, you might conclude there is little difference in dissolved solids from mid-summer through fall because stream discharge remains fairly constant. Therefore minimal sampling during this time should describe the discharge-dissolved solids relationship.

Or you might construct a simple diagram of the visitor or population curve as a function of season for a study to determine the influence of domestic waste discharged from a resort area to a river, and sample accordingly.

Discuss any assumptions that underlie the design.

Indicate how the design relates to the study objectives and to characteristics of the site/area described in the background information.

Explain how the proposed sampling frequency and locations relate to the expected temporal and spatial variability of the parameters of interest.

A measurement result is an estimate of the amount or concentration of the parameter being determined. The validity of that estimate is affected by the location, timing, and procedures selected for field measurements, sampling, and laboratory analyses.

Sometimes sampling locations are defined by the project objectives (e.g., characterize a specific effluent). In other cases, a sampling strategy must be developed.

Sampling may be based on probability or professional judgment. Remember that statistical methods are tools to be used in support of common sense and professional judgment, not as a substitute for either.

When decisions on sampling will be made in the field, describe the process for making those decisions.

Representativeness

Obtaining representative measurements or samples requires a good sampling design as well as good execution of that design. A result is representative of a population when it reflects accurately the desired characteristic of that population. A set of representative samples is said to be valid if it provides a true representation of the temporal and spatial variations of the population characteristic. These seem like simple concepts, but obtaining representative and valid data requires careful planning. The target population must be clearly identified in Element 4, *Project Description*. The sample must be taken, or measurement made, at the appropriate time and place using appropriate equipment and procedures. Finally, the sample must be handled in such a way that it remains unchanged until it is analyzed. Procedures for obtaining representative results are described in Element 8, *Sampling Procedures*.

The sampler must consider how a pollutant is transported through a medium and the fate of the pollutant. For example, pollutants may be entrained in different parts of an aquatic ecosystem (e.g., water, sediment, and biota). The sampler needs to identify the dynamics of the pollutant in the river, stream, or lake and focus on sampling where the pollutant is most concentrated. Designing a monitoring program that focuses on degraded portions of an aquatic environment provides a more accurate description of current conditions and a more effective cleanup.

If the order of sampling is important, it should be described here.

For example, it is usually important to collect the samples in order of suspected increasing concentration to minimize cross-contamination from the sampling equipment. When wading streams, it is important to sample downstream first to avoid contaminating the samples with re-suspended sediment from upstream. However, for time-of-travel sampling, it is necessary to sample from upstream to downstream since the objective is to sample the same block of water as it moves downstream.

Sample collection should be scheduled to best characterize the problem. For example, nonpoint impacts on water quality often are related to certain land-use activities and weather conditions. If samples are not collected when those activities are going on or during typical weather patterns, the results may not be representative of their impact on water quality. Another example is that dissolved oxygen concentrations are generally

lowest at night; therefore, samples taken in late afternoon will probably not be representative of the lowest oxygen conditions.

Be aware of ancillary parameters that are necessary to evaluate a contaminant of interest against a criterion or standard. For example, hardness is a factor in calculating the water quality standard for several metals, and pH is needed to assess toxicity.

Information on representative sampling designs is available in several references. EPA Document QA/G-5S, *Guidance for Choosing a Sampling Design for Environmental Data Collection,* provides information on environmental study design. Ecology's *Technical Guidance for Assessing the Quality of Aquatic Environments* (Ecology, 1994) includes chapters on planning and study design, water quality assessment, TMDL analysis, and biological surveys. *Guidance on Sampling and Data Analysis Methods* (Ecology, 1995) provides information for cleanup actions conducted under the Model Toxics Control Act Cleanup Regulation.

Specialists in Ecology's Environmental Assessment Program have extensive experience in sampling environmental media and can be consulted for advice.

Comparability

If you want to compare your data with other data sets, and combine those data for the decision to be made, the issue of comparability will need to be addressed in the project plan. Comparability is ensured by selecting and documenting standardized procedures for sampling and analysis, and by clearly stating any non-standard requirements.

Describe the quality objectives for comparability of data.

Then select procedures that will ensure your project data will match those objectives. These might include a requirement that the same standard operating procedures be used for all sampling and analysis. All laboratories involved in the project might be required to meet the same MQOs and use the same QC acceptance criteria. Some critical characteristics might involve the type of sampler used, the analytical or measurement method selected, holding times, and QC procedures.

Completeness

EPA has defined completeness as a measure of the amount of valid data needed to be obtained from a measurement system.

You may define an MQO for completeness in terms of the number or percentage of valid measurements needed to meet the project's objectives.

8. Sampling Procedures

The procedures selected for sampling affect the accuracy, representativeness, and comparability of your results. Sampling may account for more variability in your results than the measurement process.

A field survey may be needed in order to identify any logistical problems and hazards that can affect sampling. Sampling procedures and equipment proposed for use may also need to be tested before they are included in the project plan. You do not want to find out that the procedure or equipment does not work when you go out to collect samples for the first time.

Sample collection activities must not significantly disturb the environment being sampled. For instance, sediments in streams, lakes, and estuaries are easily resuspended; the surface microlayer concentrates some contaminants in quiet waters; and exhaust or fluids from a vehicle can contaminate your samples. These kinds of potential problems must be addressed in the planning process in order to obtain representative samples. After collection, samples must remain stable during transport and storage. Careful adherence to documented procedures for sample collection, preservation, and storage will minimize errors due to sampling and sample instability.

Describe in detail or reference the procedures for collecting samples.

Referenced SOPs or published procedures must be up-to-date and readily available. If a referenced method offers various options, specify the particular option to be used in this study. It may be useful to include SOPs as appendices to the plan to facilitate project implementation.

Stream Sampling Protocols for the Environmental Monitoring and Trends Section (Ecology, 2001) provides guidance on field sampling. The Puget Sound Water Quality Action Team publishes *Puget Sound Protocols and Guidelines* covering procedures for environmental sampling and analysis. These documents are available at the web sites listed in Appendix J.

Include a table listing containers, sample size, preservation, and holding times for each parameter.

Requirements for containers, sample size, preservation, and holding times should be discussed with the laboratory. A table with this information for different parameters and matrices is included on Ecology's website and also in the Manchester Environmental Laboratory *Lab Users Manual* (Ecology, 2003b) When planning the number of containers that are needed, be sure to include QA field samples as well as environmental samples. An example of a completed table is found in Appendix H.

Describe the procedures for decontaminating sampling equipment and disposing of waste from field operations.

Decontamination waste must be disposed of according to federal, state, and local regulations.

Describe the sample identification scheme.

List the information to be recorded on the sample labels and tags, such as:

- identifying number
- location
- date & time
- sampler's initials
- parameters
- preservatives

Plan to prepare labels, tags, and forms before you leave for the field. Duplicate labeling with sample labels and tags is recommended, since labels can smudge or detach from the container. To avoid smudging, use waterproof ink to fill out the labels and tags.

Describe the procedures and assign responsibility for transporting samples to the lab.

Make sure the samples will arrive in time for analysis before the holding times expire. Include in the plan a copy of the form, with examples of required entries, which will accompany the samples to the laboratory.

Describe or reference chain-of-custody procedures.

If your data may be needed for regulatory purposes, follow formal chain-of-custody procedures, such as those described in the Manchester Environmental Laboratory *Lab Users Manual* (Ecology, 2003b). You have custody of a sample if it is in your possession, under your control, or in a secure area with access restricted to authorized personnel.

It is recommended that detailed notes on field activities be kept in a bound notebook with consecutively numbered pages. Notebooks with waterproof paper are available for field notes. Entries should be made in permanent, waterproof ink and initialed and dated. Corrections are made by drawing a single line through the error so it remains legible, writing the corrections adjacent to the errors, and initialing the correction. These practices ensure that data are legally defensible, since all changes in the data are part of the record.

Notes on the collection and handling of samples should be sufficiently detailed to allow the data user to understand and evaluate the procedures.

Include a list of the required field log entries such as:

- Name of the project and the location
- Identity of field personnel
- Sequence of events
- Changes to the plan
- Site and atmospheric conditions
- Number of samples collected
- Date, time, location, identification, and description for each sample
- Instrument calibration procedures
- Field measurement results
- Identity of QC samples
- Unusual circumstances which affect interpretation of the data

Describe plans for taking pictures of key features of the site or of the sampling process.

Require documentation of the exact locations where the pictures were taken. This information will be particularly useful if there is a need to return and take pictures to document changes over time.

You may want to describe other activities such as:

- Briefings and training for field staff
- Periodic preventive maintenance (PM) of measurement and test equipment
- Procedures and equipment for homogenizing non-aqueous matrices
- Procedures for notifying the lab about sample shipments

9. Measurement Procedures

Measurements can be made in the laboratory or the field, and written procedures or methods need to be specified for both, preferably in the form of standard operating procedures (SOPs). A method is the set of written instructions completely defining the procedure to be used.

Before submitting samples to the laboratory, coordinate with lab staff for their services. The first contact might be a phone call or e-mail indicating what you are planning to do. If you hold a planning team meeting, include a representative from the lab. Lab staff can help select analytical methods with documented performance characteristics that meet the measurement quality objectives (MQOs) stipulated in Element 6, *Quality Objectives*.

The method(s) selected should have performance characteristics that meet the MQOs for precision, bias, and sensitivity. An important consideration is the potential bias for the analytes in the matrices of interest. Additional considerations in choosing a method include:

- Definition of the parameter and the form or forms to be measured (e.g., dissolved and total metals)
- Concentration range of interest
- Frequency of analysis and the number of samples to be analyzed per batch
- Size of sample available
- Sample preservation and holding time requirements
- Cost of analysis

For some parameters, MQOs for the lowest concentrations of interest may have been specified in Element 6. In selecting a method, the lowest concentration of interest is usually equated with the limit of detection. Consult with the laboratory to choose a method with a limit of detection at or below the specified lowest concentration of interest. There are some differences in the way laboratories determine their limit of detection. Many laboratories calculate a method detection limit (MDL) as defined by EPA.

Regardless of how the laboratory has determined its limit of detection, the important consideration is that the laboratory can routinely report results at or below your lowest concentration of interest. Recall that the lowest concentration of interest was chosen to be 10 times lower than the reference level (standard or criteria) of concern, in order to ensure precise results at the reference level. If occasionally the laboratory fails to report down to the lowest concentration of concern (due to matrix effects, for example), you may still be able to obtain usable data at or near the reference level.

Sometimes the selection of analytical methods is restricted. For example, some federal and state programs require the use of specific methods. If you plan to compare your

results with those from another study, or to conduct a trend analysis, select procedures comparable to those used previously. Another consideration in selecting an appropriate method is turnaround time (i.e., the total time necessary to analyze a sample and report the result). Some methods may not be able to meet your required turnaround time.

The method must be fully documented either in a publication or in an SOP and validated by the lab before it is used.

The Manchester Environmental Laboratory uses a *Pre-Sampling Notification* form and *Sample Container Request* form to aid in coordinating analytical services. The lab also requires that a completed copy of their *Laboratory Analyses Required* form (which also serves as the chain-of-custody form) accompany the samples. Much of the information on these forms is included in this element of the QA Project Plan.

Prepare a table with the following information:

- Analyte
- Sample Matrix
- Number of Samples and Arrival Date
- Reporting Limit
- Expected Range of Results (if known)
- Schedule of Delivery
- Analytical Method(s) (including sample preparation procedures)

An example of a completed table is found in Appendix H.

Specify sample preparation procedures if they are not included in the analytical method or when multiple options are offered in the method.

Describe or reference any specialized procedures or modifications to established methods.

A separate table is recommended for measurements that will be done in the field.

For field measurements, some of the information in the table may not apply. Reference an SOP or other written description of the field measurement procedure. The SOP should include the procedures for calibration and analysis. If an instrument is used, specify the manufacturer and model. Describe QC procedures that will be used to check the accuracy of measurement, along with the frequency of the checks.

Some projects require rapid turnaround on-site measurements. If many measurements at low cost can be done, the method selected may not need to be as precise as a more costly laboratory method. The rationale for this approach is explained under the precision heading in the Addendum to Element 6, *Quality Objectives*.

Ecology Policy 1-22 requires that data from analyses of "water, sediment, sludge, air, soil, plant and animal tissue, and hazardous waste" come from laboratories accredited for the parameters and methods used. Contact Ecology's Environmental Assessment Program Lab Accreditation Section for information on accredited labs. A list of accredited labs is available at the web site listed in Appendix J.

Keep in mind that accreditation means that the lab has the capability to provide accurate data. However, MQOs must be specified to ensure that the laboratory uses methods and QC procedures appropriate to meet the needs of your project. The specification of MQOs and the use of QC procedures are always required to ensure the quality of your data.

A list of available methods at the Manchester Laboratory can be found at the intranet site listed in Appendix J and also in the *Lab Users Manual* (Ecology, 2003b). Standard operating procedures corresponding to these methods are maintained by the laboratory. Other methods may be available by special request. In addition, analyses by other methods may be contracted by the laboratory. The project manager should contact the laboratory with any questions related to analytical methods and sample shipment. Ecology QA staff (agency QA Officer as well as program and lab QA Coordinators) may be able to advise you on method selection and applicability.

If analytical services are contracted to private laboratories, be sure that all state and agency requirements for purchasing products or services are followed.

In some cases, competitive bidding requirements for contracts mean that the QA Project Plan is prepared before it is known which laboratory will perform the work. In those cases, a consultant with expertise in environmental analyses may be engaged, the plan may be revised, or a lab addendum may be prepared after the laboratory becomes part of the project team.

10. Quality Control

Quantitative measurement quality objectives (MQOs) are established in Element 6, *Quality Objectives*. The results for quality control (QC) samples are used to evaluate whether the measurement system is functioning properly and whether the MQOs have been met. QC requirements should be specified for both laboratory and field measurements, although more QC can generally be implemented for analyses done in a controlled laboratory environment. Recent versions of most analytical methods specify that control limits be based on historical lab performance, while some specify fixed values for QC limits. An important consideration stated by Crumbling (2001) is that "QC acceptance criteria should be very specific and should be designed such that if the QC acceptance criteria are consistently met, the project MQOs will be achieved."

Prepare a table listing the types and frequency of field and laboratory QC samples required for the study.

An example of a completed table is given in Appendix H.

The following discussion is intended to assist you in preparing the table and understanding the different types of QC samples that can be specified.

Analytical QC

Many analytical methods include a section on QC procedures. The project manager should be familiar with the terminology and theory of analytical QC so as to be able to discuss them with lab staff. The Ecology QA Officer and program and lab QA Coordinators may be able to help with this communication.

Analytical QC procedures involve the use of four basic types of QC samples. QC samples are analyzed within a batch of client samples to provide an indication of the performance of the entire analytical system. Therefore, QC samples go through all sample preparation, clean up, measurement, and data reduction steps in the procedure. In some cases, the laboratory may perform additional tests that check only one part of the analytical system.

Note that the analysis of calibration standards is not considered part of QC, since all methods must include calibration whether or not QC samples are analyzed. A discussion of calibration is included in Appendix I.

Check standards

Check standards are QC samples of known concentration prepared independently of the calibration standards. They are sometimes called laboratory control samples (LCS) or spiked blanks. Results are used to verify that analytical precision is in control and that the level of bias due to calibration is acceptable. If the results for the check standards do not fall within established control limits, the measurement system should be re-calibrated.

In some analytical methods, sample results may be qualified when associated check standard results are not within acceptable limits.

Check standards are usually prepared in deionized water, though any uncontaminated medium can be used. Their concentration should be in the range of interest for the samples, and at least one check standard should be analyzed with each batch of 20 samples or fewer.

Reference materials that more closely match the matrix of environmental samples may be used as check standards for your project. Some proficiency testing (PT) samples from commercial vendors can be stored and used as check standards once the true values are known. The acceptance limits for the results of analyses of these commercial samples should not be those set by the vendor but should be established in the lab by replicate analyses of the PT sample. An exception is when reference materials are sent to the laboratory for analysis as blinds. Ecology's Laboratory Accreditation Section can help identify suppliers of PT samples and certified reference materials.

Analytical duplicates

The laboratory analyzes duplicate aliquots of one or more samples within each batch. Results are used to estimate analytical precision for that matrix at that concentration.

The project manager may specify which samples are to be analyzed in duplicate.

If the samples selected for duplicate analyses do not contain measurable amounts of the analyte of interest, the results provide no information on precision. Also, if the lab selects samples from another study with significantly different levels of the analyte or different matrices, the estimate of precision may not be applicable to your samples.

One of the field duplicates is a good choice for an analytical duplicate since you may then estimate total and analytical variability from results for the same sample. There is no advantage to "randomly" selecting samples for duplicate analysis.

Matrix spikes

A matrix spike is an aliquot of a sample to which a known amount of analyte is added at the start of the procedure. Matrix spike recoveries may provide an indication of bias due to interference from components of the sample matrix.

Since the percent recovery is calculated from the difference between the analytical results for the spiked and unspiked samples, its precision may be relatively poor. If the spike is too high relative to the sample concentration, any interference effect at the sample concentration level could be masked. And if too low, random error would make it difficult to accurately estimate the recovery. The aim should be to spike at a concentration approximately equal to the concentration in the sample before spiking.

The project manager may indicate to the laboratory which samples might be most appropriate for use as matrix spikes and, if necessary, provide larger samples for this purpose.

In some cases, many replicate spikes would need to be analyzed in order to distinguish bias from the effects of random error on the recoveries. Thus, matrix spike results are not used to correct sample results and should only be used in conjunction with other QC data to qualify them.

While the primary use of matrix spikes is to indicate the presence of bias, duplicate spike results can be used to estimate analytical precision at the concentration of the spiked samples.

The project manager may instruct the laboratory to spike certain samples since matrix spikes are not automatically included in all analytical methods.

If the laboratory does not receive instructions, they may choose not to do any analyses of spiked samples or may select samples from other projects for spiking. Matrix spikes prepared from other types of samples or matrices provide no information on bias due to the matrices in your samples.

Some methods for organics analyses specify that all samples, including QC samples, be spiked with surrogate compounds at the start of the procedure. Because surrogate compounds are not expected to be present in the samples, they give analytical responses that can be distinguished from those of the analytes of interest. Surrogate recoveries provide an estimate of accuracy for the entire analytical procedure. The standard deviations of surrogate results provide an estimate of analytical precision, while the mean percent recoveries indicate whether or not the sample results are biased.

Laboratory blanks

Blanks are prepared and analyzed in the laboratory to document the response of the measurement system to a sample containing effectively none of the analyte of interest. They should not be confused with field blanks that are analyzed to determine if there is contamination during sampling. Depending on the analytical method, the analyst will analyze one or more blanks with each batch of samples and compare the results to established acceptance limits.

A positive blank response can be due to a variety of factors related to the procedure, equipment, or reagents. Unusually high blank responses indicate laboratory contamination. The blank response becomes very important when the analyte concentration is near the detection limit. Blank responses are sometimes used to correct the sample responses and to determine the limit of detection.

Field QC

The project manager is responsible for selecting QC procedures to be used in the field. Field QC samples may be sent to the laboratory as blinds (i.e., identified the same way as normal samples) to ensure that they are not treated differently during analysis.

Replicates

Replicates are two (duplicates) or more samples collected, or measurements made, at the same time and place. Replicate results provide a way to estimate the total random variability (precision) of individual results. If conditions in the medium being measured or sampled are changing faster than the procedure can be repeated, then the precision calculated from replicate results will include that variability as well. Appendix G describes the calculation of precision from replicate results.

Replicate results that are "non-detects" cannot be used to estimate precision. Since there is no advantage to randomly selecting samples for replication, use all available information and professional judgment to select samples or measurements likely to yield positive results.

Samples are sometimes split in the field and sent to separate laboratories for analysis. This has been common practice in compliance situations. However, you should be aware of the limitations of this practice, since there is no way to determine which result is correct when they do not agree. No laboratory, however good their reputation, can be considered correct by definition. If the project manager doubts the lab's ability to meet the MQOs, those concerns should be resolved through analyses of representative samples and reference materials or proficiency testing samples before any commitment is made for analysis of study samples.

Field blanks

Field blanks are samples of "clean" material which are exposed to conditions in the field. They should be analyzed like any other sample. The results for field blanks may indicate the presence of contamination due to sample collection and handling procedures (in the field or during transport to the laboratory) or to conditions in the field, such as boat or vehicle exhaust. Plan to clearly identify field blanks so that they are not selected for analytical duplicates or matrix spikes.

Field blanks are used when there is reason to expect problems with contamination or to meet programmatic or contractual requirements to demonstrate absence of contamination**.** The use of good operational procedures in the field and thorough training of field staff reduces the risk of contamination.

Several types of field blanks are described below. The pure water or other "clean" material used to prepare them must be obtained from the laboratory or other reliable supplier.

- A *transport blank* is a container of pure water, which is prepared at the lab and carried unopened to the field and back with the other sample containers to check for possible contamination in the containers or for cross-contamination during transportation and storage of the samples.

- A *transfer blank* is prepared by filling a sample container with pure water during routine sample collection to check for possible contamination from the surroundings. The transfer blank will also detect contamination from the containers or from cross-contamination during transportation and storage of the samples.

- A *rinsate (equipment) blank* is prepared by exposing clean material to the sampling equipment after the equipment has been used in the field and cleaned. The results provide a check on the effectiveness of the cleaning procedures. The rinsate blank may also detect contamination from the surroundings, from containers, or from cross-contamination during transportation and storage of the samples and is therefore the most comprehensive type of field blank.

- A *filter blank* is a special case of a rinsate blank prepared by filtering pure water through the filtration apparatus after routine cleaning. The filter blank may detect contamination from the filter or other part of the filtration apparatus.

Ideally, the results for your field blanks will be "not detected." If the results are positives, you will need to take them into account when reporting sample results and determining whether your MQOs have been met.

Check standards

Check standards and spiked samples usually are not prepared in the field due to the hazards of working with concentrated solutions of contaminants under field conditions.

In some projects, it may be useful to acquire check standards to be sent to the laboratory for analysis along with the environmental samples. These can be PT samples or certified reference materials, and the laboratory results are compared with the acceptance limits of the provider.

Describe the field QC procedures to be used for the study.

Specify the number of each type of QC sample to be included in the study. For field blanks, specify also the source of "clean" material (e.g., pure water) that will be used.

Corrective Actions

QC results may indicate problems with data during the course of the project. The lab will follow prescribed procedures to resolve the problems. Options for corrective action might include:

- Retrieving missing information
- Re-calibrating the measurement system
- Re-analyzing samples (must be done within holding time requirements)
- Modifying the analytical procedures
- Collecting additional samples or taking additional field measurements
- Qualifying results

Describe in your project plan any additional procedures to be followed to correct or compensate for QC problems if they occur.

11. Data Management Procedures

Data management addresses the path of data from recording in the field or laboratory to final use and archiving. Experience has shown that roughly half of the errors in results reported for proficiency testing (PT) samples have been due to mistakes in recording results, calculations, or transcription.

Describe the procedures for recording and reporting data acquired in the field.

Include procedures for detecting and correcting errors and for compiling and analyzing the data, including software requirements.

Describe requirements for the data package from the laboratory.

Documentation should always include a case narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers.

The lab data package should also include all QC results associated with your data. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met. This should include results for all blanks, surrogate compounds, and check standards included in the sample batch, as well as results for analytical duplicates and matrix spikes prepared from your samples.

List requirements for electronic transfer of data from the field or lab to your database.

Provide or reference information necessary to enter the data in your information management system. The Environmental Information Management (EIM) system is the major environmental data repository for Ecology. Information on the EIM system is available on Ecology's internet web site listed in Appendix J.

Describe procedures for obtaining data from existing databases and literature files.

List acceptance criteria for these data in terms of precision, bias, sensitivity, representativeness, comparability, and completeness. Discuss any qualifiers associated with the data.

12. Audits and Reports

A process is needed to ensure that the QA Project Plan is implemented correctly, that the quality of the data is acceptable, and that corrective actions are implemented in a timely manner.

Audits

Two types of useful audits are:

- *Technical Systems Audit* – a qualitative audit of conformance to the QA Project Plan. The audit is conducted soon after work has commenced, so that corrective actions can be implemented early in the project.
- *Proficiency Testing* – the quantitative determination of an analyte in a blind standard to evaluate the proficiency of the analyst or laboratory.

Describe any audits that will be conducted during the project.

Discuss the purpose and scope of each audit and identify the auditors. Provide the schedule and describe how the results will be reported.

Reports

Project plans for large or repetitive projects should describe a mechanism for periodic reports to management on the performance of measurement systems and on data quality. These reports may include:

- Assessment of data accuracy and completeness
- Results of proficiency testing and/or technical systems audits
- Significant QA problems and corrective actions taken
- Any other information requested by management

List the reports required for the project and identify staff responsible for preparing them.

The final report for each project should include a QA section that describes data quality. The final report should undergo peer review, a scientific review of the report by staff with appropriate expertise who are not directly connected with the project. Peer reviews ensure that project activities were technically sound and properly documented. Guidelines for technical document review are provided on the Ecology intranet site listed in Appendix J.

13. Data Verification and Validation

Assessment is the process by which data are examined and evaluated to varying levels of detail and specificity. It includes verification, validation, and data quality assessment. This element covers the steps of data verification and validation. The data quality assessment step, covered in Element 14, is done on data that have been verified and validated (i.e., data of known and documented quality).

Data verification involves examining the data for errors or omissions as well as examining the results for compliance with QC acceptance criteria. Laboratory results are reviewed and verified by qualified and experienced lab staff. Their findings are documented in the case narrative. Field results should also be verified, preferably before leaving the site where the measurements were made.

Once the measurement results have been recorded, they are verified to ensure that:

- Data are consistent, correct, and complete, with no errors or omissions
- Results for QC samples described in Element 10, *Quality Control,* accompany the sample results
- Established criteria for QC results were met
- Data qualifiers are properly assigned where necessary
- Data specified in Element 7, *Sampling Process Design,* were obtained
- Methods and protocols specified in the QA Project Plan were followed

Describe the procedures for verifying results for measurements done in the laboratory and in the field, and assign responsibility for verification.

Data validation is an analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the analytical quality of a specific data set. It involves a detailed examination of the data package using professional judgment to determine whether the MQOs for precision, bias, and sensitivity have been met. Validation is the responsibility of the project manager, who may wish to arrange for a qualified specialist to conduct the validation and document it in a technical report. Sometimes validation can be streamlined by validating only a specific percentage of all data sets unless a problem is identified; this may include a caveat that all critical samples identified will undergo full data validation.

The results of QC sample analyses can often be compared directly to the MQOs to determine whether they have been met. For projects that follow the WRC approach described in Appendix F, an experimental design for preliminary estimation of precision and bias, and the use of control charts, provide an excellent way to determine if MQOs have been met.

Describe the procedures to be used for data validation.

14. Data Quality (Usability) Assessment

After the data have been verified and validated, Data Quality Assessment (DQA) or Usability Assessment is done. If the MQOs have been met, the quality of the data should be useable for meeting project objectives. If the MQOs have not been met for data (i.e., data have been qualified), you need to determine if they are still useable. You also need to determine if the quantity of data is sufficient to meet project objectives. This includes an assessment of whether the requirements for representativeness and comparability have been met. If you set an MQO for completeness, compare the number of valid measurements completed with those established by the MQO. And you need to evaluate whether the implementation of the sampling design gave the information expected for meeting project objectives.

DQA is built on a fundamental premise: data quality is meaningful only when it relates to the *intended* use of the data. DQA determines whether the study questions can be answered and the necessary decisions made with the desired confidence.

While it may not be possible during the planning phase to anticipate everything you will need to do when analyzing the data, it pays to include in your project plan as much detail as possible about how you will assess the usability of the data and what graphical and statistical tools you will use to determine if the project objectives have been met.

State how you will assess the data to determine if they are of the right type, quality, and quantity to support the project objectives.

Summarize the methods you will use in the analysis and presentation of the data.

Describe any statistical calculations and graphical representations you plan on doing.

This may involve statistical tests and verification of the assumptions of the statistical tests (e.g., tests of hypotheses, tests for outliers, tests for trends), as well as scientific evaluation of the information.

Describe how the data will be presented (e.g., tables or charts) to illustrate trends, relationships and anomalies, and how you will handle data below the lower reporting limit or detection limit.

State how you will evaluate the data to determine if the sampling design has been adequate and if it needs any modification for future use.

It is important to evaluate whether the sampling design can be used over a wide range of possible outcomes.

Finally, indicate who will be responsible for analyzing the data and how the results of the data analysis will be documented.

If you have used either the DQO Process or PAC Process for systematic planning, you can use the DQA Process to determine whether the objectives of the project have been met. While the DQA Process was developed to evaluate data from the DQO Process, it can be adapted to the PAC Process or other systematic planning process.

The DQA Process involves the following steps:

1. Review the project objectives and sampling design
2. Conduct a preliminary data review
3. Select the statistical method
4. Verify the assumptions of the statistical method
5. Draw conclusions from the data

EPA document QA/G-9, *Guidance for Data Quality Assessment,* provides background information and statistical tools for performing each of the steps in the DQA Process. EPA has plans to split this document into a statistical guidance document and a guide for managers.

In the DQO Process, quality objectives are specified at both the level of the decision and the level of the measurements needed to support the decision or study question, while in the PAC Process, quality objectives are only specified at the level of the measurements. Thus, data analysis is generally more involved for the DQO Process.

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EPA Quality System Documents

www.epa.gov/quality/qa_docs.html

EPA QA/G-1	*Guidance for Developing Quality Systems for Environmental Programs*
EPA QA/R-2	*EPA Requirements for Quality Management Plans*
EPA QA/G-3	*Guidance on Assessing Quality Systems*
EPA QA/G-4	*Guidance for the Data Quality Objectives Process*
EPA QA/G-4D	*Decision Error Feasibility Trials (DEFT) Software*
EPA QA/G-4HW	*Data Quality Objectives Process for Hazardous Waste Site Investigations*
EPA QA/R-5	*EPA Requirements for Quality Assurance Project Plans*
EPA QA/G-5	*Guidance for Quality Assurance Project Plans*
EPA QA/G-5G	*Guidance for Geospatial Data Quality Assurance Project Plans*
EPA QA/G-5M	*Guidance for Quality Assurance Project Plans for Modeling*
EPA QA/G-5S	*Guidance on Choosing a Sampling Design for Environmental Data Collection*
EPA QA/G-6	*Guidance for Preparation of Standard Operating Procedures*
EPA QA/G-7	*Guidance on Technical Audits and Related Assessments for Environmental Data Operations*
EPA QA/G-8	*Guidance on Environmental Data Verification and Data Validation*
EPA QA/G-9	*Guidance for Data Quality Assessment: Practical Methods for Data Analysis*
EPA QA/G-10	*Guidance for Developing a Training Program for Quality Systems*

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FR, 40CFR58, Subpart G, Appendix B - Quality Assurance Requirements for Prevention of Significant Deterioration (PSD) Air Monitoring. Federal Register.

FR, 40CFR60. Appendix E - Quality Assurance Requirements for Continuous Emission Monitoring Systems (CEMS), to be submitted as a proposed regulation to amend 40 CFR 60. Federal Register.

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Appendices

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Appendix A

Glossary

Accreditation - "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data…(Ecology) does not, by certifying or accrediting any laboratory…vouch for or warrant the accuracy of any particular work done or report issued by the laboratory." [WAC 173-50-040]

Accuracy - An estimate of the closeness of a measurement result to the true value.

Bias - The difference between the population mean and the true value.

Blank - A sample prepared to contain none of the analyte of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample.

Calibration - The process of establishing the relationship between the response of a measurement system and the value of the parameter being measured.

Check standard - A QC sample prepared independently of calibration standards and analyzed along with the samples to check the precision of the measurement system. A check standard can also be used to check for bias due to the way calibration is done. It is sometimes called a lab control sample (LCS) or spiked blank.

Control chart - A graphical representation of the precision of QC results showing whether the measurement system is in statistical control.

Control limits - Statistical warning and action limits calculated for control charts.

Data Quality Objectives Process – EPA's recommended systematic planning process when environmental data are used to decide between two opposing conditions (e.g., compliance or non-compliance with a standard).

Data validation - An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the analytical quality of a specific data set. It involves a detailed examination of the data package using professional judgment to determine whether the MQOs for precision, bias, and sensitivity have been met.

Data verification - Examination of the data for errors or omissions and of the QC results for compliance with acceptance criteria.

Detection limit (limit of detection) - The concentration or amount of an analyte which, on an "a priori" basis, can be determined to a specified level of certainty to be greater than zero.

Duplicates - Two samples collected or measurements made at the same time and location, or two aliquots of the same sample prepared and analyzed in the same batch.

Field blank - A blank used to obtain information on contamination introduced during sample collection, storage, and transport.

Laboratory control sample (LCS) - See "Check standard."

Matrix spike - A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects.

Measurement quality objectives (MQOs) - The performance or acceptance criteria for individual data quality indicators, including precision, bias, and sensitivity.

Measurement result - A value obtained by carrying out once the procedure described in a method.

Method - A set of written instructions completely defining the procedure to be used.

Method blank - A blank prepared to represent the sample matrix and analyzed in a batch of samples.

PAC Process - The recommended systematic planning process when decision-making is not the primary focus of the data collection activity.

Parameter - A specified characteristic of a population or sample.

Population - The hypothetical set of all possible observations of the type which is being investigated.

Precision - A measure of the variability in the results of replicate measurements due to random error.

Quality assurance (QA) - Adherence to a system for assuring the reliability of measurement data.

Quality assurance project plan (QA Project Plan) - A document that describes the objectives of a project and the procedures necessary to acquire data that will serve those objectives.

Quality control (QC) - The routine application of statistical procedures to evaluate and control the accuracy of measurement data.

Relative percent difference (RPD) - The difference between two values divided by their mean and multiplied by 100.

Replicates - Two or more samples collected or measurements made at the same time and place.

Sensitivity - In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit.

Standard operating procedure (SOP) - A document that describes in detail the approved way for performing a routine procedure.

Systematic planning - A step-wise process of clearly describing the goals and objectives of a project, and deciding on the types and amounts of data that will be needed to meet those goals and objectives.

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Appendix B

Systematic Planning

Systematic planning is a step-wise process of clearly describing the goals and objectives of a project, and deciding on the types and amounts of data that will be needed. Characteristics of systematic planning include involvement of all interested parties, definition of the quality of data appropriate for their intended use, and use of the scientific method (observation, hypothesis, and testing).

EPA describes the elements of a systematic planning process as:

1. Establishment of a team (identification of the project manager, sponsoring organization, staff, interested parties, and experts)
2. Description of the project goal, objectives, and questions and issues to be addressed
3. Identification of project schedule, resources (including budget), milestones, and any applicable requirements (e.g., regulatory requirements, contractual requirements)
4. Description of the type of data needed to meet the project objectives
5. Description of the data collection and analysis requirements
6. Description of the process for the generation, evaluation, and assessment of collected data

The systematic planning process is the foundation of the planning stage; outputs of the process are documented in the QA Project Plan. Those outputs include performance and acceptance criteria for the quality of the data collected and objectives for the quality of the decision, as described in EPA QA/G-5.

Performance criteria address the adequacy of new data collected specifically for the project.

Acceptance criteria address the adequacy of existing data proposed for inclusion in the project.

The Data Quality Objectives Process

EPA has developed a seven-step systematic planning process called the Data Quality Objectives (DQO) Process for use when data are being used to select between two clear alternative conditions or to determine compliance with a standard. As such, a better name would be the *Decision* Quality Objectives Process. It is EPA's recommended systematic planning tool, and they have provided guidance for its use (*Guidance for the Data Quality Objectives Process, EPA QA/G-4 and Data Quality Objectives Process for Hazardous Waste Site Investigations, EPA QA/G-4HW*). Since the DQO Process is used to facilitate decision-making, an alternative name is the Decision Quality Objectives Process.

The DQO Process consists of the following steps:

1. State the problem
2. Identify the decision
3. Identify the inputs to the decision
4. Define the boundaries of the study
5. Develop a decision rule
6. Specify tolerable limits on decision errors
7. Optimize the design for obtaining data

One important application is to decide whether a site is contaminated and needs to be cleaned up. When critical environmental decisions need to be made, consider using the DQO Process.

In the DQO Process, quality objectives need to be specified at two levels:

1. At the level of the decision
2. At the level of the measurements used to support the decision or study question

At the level of the decision, there is a need to specify *tolerable limits of making decision errors*. These tolerable limits are required, along with other information, to determine the numbers and locations of samples from the site that must be collected and analyzed.

At the level of measurements used to support the decision or study question, quality objectives are expressed as measurement quality objectives or MQOs. The MQOs are performance or acceptance criteria for the data quality indicators precision, bias, and sensitivity.

The phrase *data quality objectives* was originally used by EPA to represent generic quality criteria for environmental data. In 1998, *data quality objectives* was replaced with *acceptance and performance criteria*, and the phrase *data quality objectives* was redefined to solely represent the outputs of the DQO Process. To avoid confusion, the expression *Decision Quality Objectives* has been used in the main text of this document to represent the outputs of the DQO Process. This is consistent with the fact that the DQOs themselves should not attempt to directly define the specifics of the data quality, as explained in the article by Crumbling (2001).

Two software tools are available to facilitate use of the DQO Process. The EPA has PC-based software for determining the feasibility of data quality objectives defined using the DQO Process. The software and the user's guide are available through the Quality System website listed in Appendix J. Visual Sample Plan (VSP) software is available free through the Pacific Northwest National Laboratory website. It is intended to help you determine the number of samples needed and where they should be taken.

Other systematic planning processes that are used to decide between two opposing conditions have been adopted by other federal agencies, and differ somewhat from EPA's DQO Process. For example, the U.S. Army Corps of Engineers adopted a four-step Technical Planning Process to implement systematic planning for contaminated site cleanup activities.

The Performance and Acceptance Criteria Process

Sometimes decision-making is not the primary focus or intended outcome of data collection, and instead data are used for descriptive purposes, to generate estimates, or to support inferences. Examples are surveys or exploratory investigations, monitoring, research studies, risk assessment studies, and modeling. In those instances, the Performance and Acceptance Criteria (PAC) Process, which uses performance and acceptance criteria as quality objectives, can be used as an alternative systematic planning process. In the PAC process, quality objectives need to be specified only at the level of the measurements used to support the study question, and are similar to the 2nd level of quality objectives for the DQO Process. These quality objectives are expressed as measurement quality objectives or MQOs.

There are seven steps in the PAC Process:

1. State the problem
2. Identify the study question
3. Identify types of information needed
4. Establish study design constraints
5. Specify information quality
6. Develop a strategy for information synthesis
7. Optimize the design for collecting information

EPA is in the process of editing the QA/G-4 document, *Guidance on the Data Quality Objectives Process,* to incorporate performance and acceptance criteria as applied to simple estimation problems, as another way of looking at the DQO Process. This modified DQO Process will likely be the same as the PAC Process described here.

The Triad Approach

The Triad Approach has been developed by the EPA's Office of Solid Waste and Emergency Response to plan and implement data collection and technical decision-making at hazardous waste sites. It is a three-pronged approach that includes systematic project planning, a dynamic work strategy, and real-time measurements. The cornerstone of the Triad is the explicit identification and management of decision uncertainties to improve the cost-effectiveness of hazardous waste site cleanups. Detailed information on the Triad Approach can be found at the EPA web address listed in Appendix J.

The SAFER Approach

The U.S. Department of Energy (DOE) developed the Streamlined Approach for Environmental Restoration (SAFER) as a methodology tailored to the challenges of conducting environmental restoration efforts under conditions of significant uncertainty. It combines the DQO Process with an Observational Approach (OA). The basis of the OA is the observational method, a technique originally developed to manage uncertainty in the design and construction of subsurface facilities such as tunnels, and allows remedial action to be initiated without full characterization of the nature and extent of the contamination.

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Appendix C

QA Project Plan Review Checklist

REVIEWER _____ DATE _____

ELEMENT	YES	COMMENTS
1 Title Page with Approvals	____	_____
Title, author, organization	____	_____
Date prepared or revised	____	_____
Approval signatures with dates	____	_____
Other signatures, as needed	____	_____
2 Table of Contents and Distribution List	____	_____
3 Background	____	_____
Study area and surroundings	____	_____
Logistical problems	____	_____
History of study area	____	_____
Contaminants of concern	____	_____
Results of previous studies	____	_____
Regulatory criteria or standards	____	_____
4 Project Description	____	_____
Project goals	____	_____
Project objectives	____	_____
Information needed and sources	____	_____
Target population	____	_____
Study boundaries	____	_____
Tasks required	____	_____
Practical constraints	____	_____
Systematic planning process used	____	_____

QA Project Plan Review Checklist (cont.)

ELEMENT	YES	COMMENTS
5 Organization and Schedule	____	_____
Key individuals and their responsibilities (project team, decision-makers, stakeholders, lab, etc.)	____	_____
Organization chart	____	_____
Project schedule	____	_____
Limitations on schedule	____	_____
Budget and funding	____	_____
6 Quality Objectives	____	_____
Decision Quality Objectives	____	_____
Measurement Quality Objectives		
Table of targets for:		
Precision	____	_____
Bias	____	_____
Sensitivity	____	_____
7 Sampling Process Design	____	_____
Study Design		
Sampling location and frequency	____	_____
Parameters to be determined	____	_____
Field measurements	____	_____
Maps or diagrams	____	_____
Assumptions underlying design	____	_____
Relation to objectives and site characteristics	____	_____
Characteristics of existing data	____	_____
8 Sampling Procedures	____	_____
Measurement and sample collection	____	_____
Containers, preservation, holding times	____	_____
Equipment decontamination	____	_____
Sample ID	____	_____
Chain-of-custody, if required	____	_____
Field log requirements	____	_____
Other activities	____	_____

QA Project Plan Review Checklist (cont.)

ELEMENT	YES	COMMENTS
9 Measurement Methods	____	_____
Lab procedures table, including	____	_____
Analyte	____	_____
Matrix	____	_____
Number of samples	____	_____
Expected range of results	____	_____
Analytical method	____	_____
Sensitivity	____	_____
Sample preparation method	____	_____
Special method requirements	____	_____
Field procedures table	____	_____
10 Quality Control	____	_____
Table of lab and field QC required	____	_____
Corrective action	____	_____
11 Data Management Procedures	____	_____
Data recording/reporting requirements	____	_____
Lab data package requirements	____	_____
Electronic transfer requirements	____	_____
Acceptance criteria for existing data	____	_____
12 Audits and Reports	____	_____
Number, frequency, type, and schedule of audits	____	_____
Responsible personnel	____	_____
Frequency and distribution of reports	____	_____
Responsibility for reports	____	_____
13 Data Verification and Validation	____	_____
Field data verification, requirements, and responsibilities	____	_____
Lab data verification	____	_____
Process for data validation	____	_____

QA Project Plan Review Checklist (cont.)

ELEMENT	YES	COMMENTS
14 Data Quality (Usability) Assessment	____	_____
Process for determining whether project objectives have been met	____	_____
Data analysis and presentation methods	____	_____
Dealing with non-detects	____	_____
Evaluating the sampling design	____	_____
Documentation of assessment	____	_____

Appendix D

Comparison of QA Project Plan Elements for EPA and Ecology

This appendix lists the elements required for QA Project Plans prepared for EPA projects and then compares the elements in this document to these EPA requirements.

EPA Document QA/G-5

A. Project Management

- A1 Title and Approval Sheet
- A2 Table of Contents
- A3 Distribution List
- A4 Project/Task Organization
- A5 Problem Definition/Background
- A6 Project/Task Description
- A7 Quality Objectives and Criteria for Measurement Data
- A8 Special Training Needs/Certification
- A9 Documents and Records

B. Data Generation and Acquisition

- B1 Sampling Process Design (Experimental Design)
- B2 Sampling Methods
- B3 Sample Handling and Custody
- B4 Analytical Methods
- B5 Quality Control
- B6 Instrument/Equipment Testing, Inspection, and Maintenance
- B7 Instrument/Equipment Calibration and Frequency
- B8 Inspection/Acceptance of Supplies and Consumables
- B9 Non-Direct Measurements
- B10 Data Management

C. Assessment/Oversight

- C1 Assessments and Response Actions
- C2 Reports to Management

D. Data Validation and Usability

- D1 Data Review, Verification, and Validation
- D2 Verification and Validation Methods
- D3 Reconciliation with User Requirements

Ecology Guidelines

In this document, most of EPA's 24 elements have been incorporated into the 14 elements as shown below. EPA elements A8 and B8 are omitted since they are not relevant to projects of the scale conducted by or for Ecology. The contents of EPA elements A9 and B9 are incorporated into various elements of this document.

Ecology Elements	EPA Elements
1. Title Page with Approvals	A1
2. Table of Contents and Distribution List	A2, A3
3. Background	A5
4. Project Description	A6
5. Organization and Schedule	A4
6. Quality Objectives	A7
7. Sampling Process Design (Experimental Design)	B1
8. Sampling Procedures	B2, B3, B6, B7
9. Measurement Procedures	B4
10. Quality Control	B5
11. Data Management Procedures	B10
12. Audits and Reports	C1, C2
13. Data Verification and Validation	D1, D2
14. Data Quality (Usability) Assessment	D3

Appendix E

Effects of Errors on Decision-making

A decision error occurs when the sample data lead to an incorrect decision. Decision errors occur because the data are incomplete and imperfect. The combination of all the errors affecting your decision is called the *total study error* or *total variability*.

Total study error consists of statistical sampling error and measurement error. Statistical sampling error occurs when the sampling design is not able to characterize fully the variability of the population over space and time, including any inherent variability (e.g., stratification) in the media being sampled. Measurement error occurs during the process of collecting, handling, and analyzing samples.

The following discussion is focused primarily on measurement error, but reference is also made on how to improve sampling design by increasing the number of samples taken and analyzed.

In keeping with the purpose of this guidance document, emphasis is placed on how planning should take into account the effects of errors on decision-making

Comparison of a Result with a Fixed Numerical Value

It is often necessary in environmental decision-making to compare a result with a fixed numerical value or action level. Examples of this are determining compliance with a water quality standard or determining whether a hazardous waste site cleanup standard has been exceeded. Projects done by or for Ecology often involve use of the data for these types of decisions.

The *Data Quality Objectives Process* described in EPA document QA/G-4 is EPA's recommended systematic planning process when data will be used to select between two alternative conditions or to determine compliance with a standard. Step 6 of the DQO Process is to specify tolerable limits on decision errors. EPA QA/G-4 provides practical guidance, but does not give a complete explanation of the statistical basis for decision-making or how the assessment decision relates to the planning process. The following provides additional information on the statistics behind EPA's process for specifying tolerable limits on decision errors.

Decisions are often made without taking into account the effect of error on those decisions. Obviously, if the results are biased (high or low), our decisions may be incorrect. Random error also needs to be taken into account when decisions are made based on environmental data.

Effect of Random Error

To begin with, assume that there is no bias in the results, only random error. This is the approach taken in the EPA QA/G-4 document. In this approach, one must take operational steps to ensure that bias in sampling and analysis is negligible. While this may not always be possible, it can provide an initial framework for the planning process.

Assume also that the results are normally distributed around a mean value, which also corresponds to the regulatory limit. Referring to Figure 1, if the action level (AL) (i.e., the maximum acceptable concentration) is set equal to that regulatory threshold (C), then when the true value equals the action level, the probability of deciding that the limit has been exceeded is 50% and equals the probability of failing to decide that the limit has been exceeded, the equivalent of flipping a coin to make a decision.

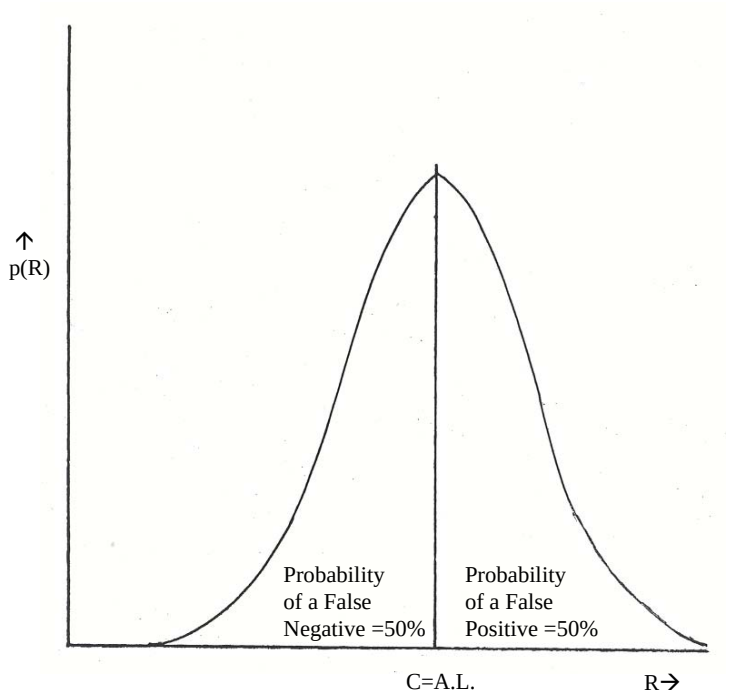

Figure 1. Effect of Random Error when the Action Level (A.L.) is Set Equal to the Regulatory Limit (C)

Often decisions are made without taking into account the probabilities of decision errors, which are referred to as *Type I* and *Type II* errors.

- Type I error is deciding that C has been exceeded when it has not. The probability of the Type I error is denoted by α.

- Type II error is the error of failing to decide that C has been exceeded when in fact it has been. The probability of the Type II error is denoted by β, and hence $(1-\beta)$ is called the power of the test (i.e., in this example, the power to determine that a standard has been exceeded).

In EPA document QA/G-4, Type I and Type II errors are defined in terms of the null hypothesis. A false rejection (Type I) decision error occurs if the decision-maker rejects the null hypothesis when it is really true, and a false acceptance (Type II) decision error occurs if the decision-maker fails to reject the null hypothesis when it is really false.

To further clarify this, consider the following cases. Figure 2(a) shows that when the true concentration of a parameter, T, is slightly less than the standard or regulatory threshold, C, random errors will frequently lead to a result, R, that is greater than C. Similarly, Figure 2(b) shows that when T is a little greater than C, there is a substantial probability that a result less than C will be obtained. Suppose the decision rule is to take corrective action whenever R>C. When T is close to C, there are significant probabilities that action will be taken when it is not necessary (when R>C but $T \leq C$) or that action will not be taken when it is required (when $R \leq C$ but T>C).

Suppose that we want to reduce the probabilities of these two undesirable decisions so that neither of them occurs at a frequency greater than 5%. To do that, a new action limit C' must be defined and action taken whenever R>C'. (See Figure 2(c).) The value of C' is chosen so that, when T=C, the probability of obtaining a result less than C' is no greater than 0.05. From the properties of the normal distribution, $C'=C-1.64\sigma_C$, where σ_C is the standard deviation of measurement results at the level C.

However when T=C', action will be called for needlessly 50% of the time. Thus, to ensure that action is not needlessly taken too frequently, the aim must be to make the decision at or below a control limit C", where C" is chosen so that, when T=C", the probability of obtaining a result greater than C' is no more than 0.05. (See Figure 2(d).)

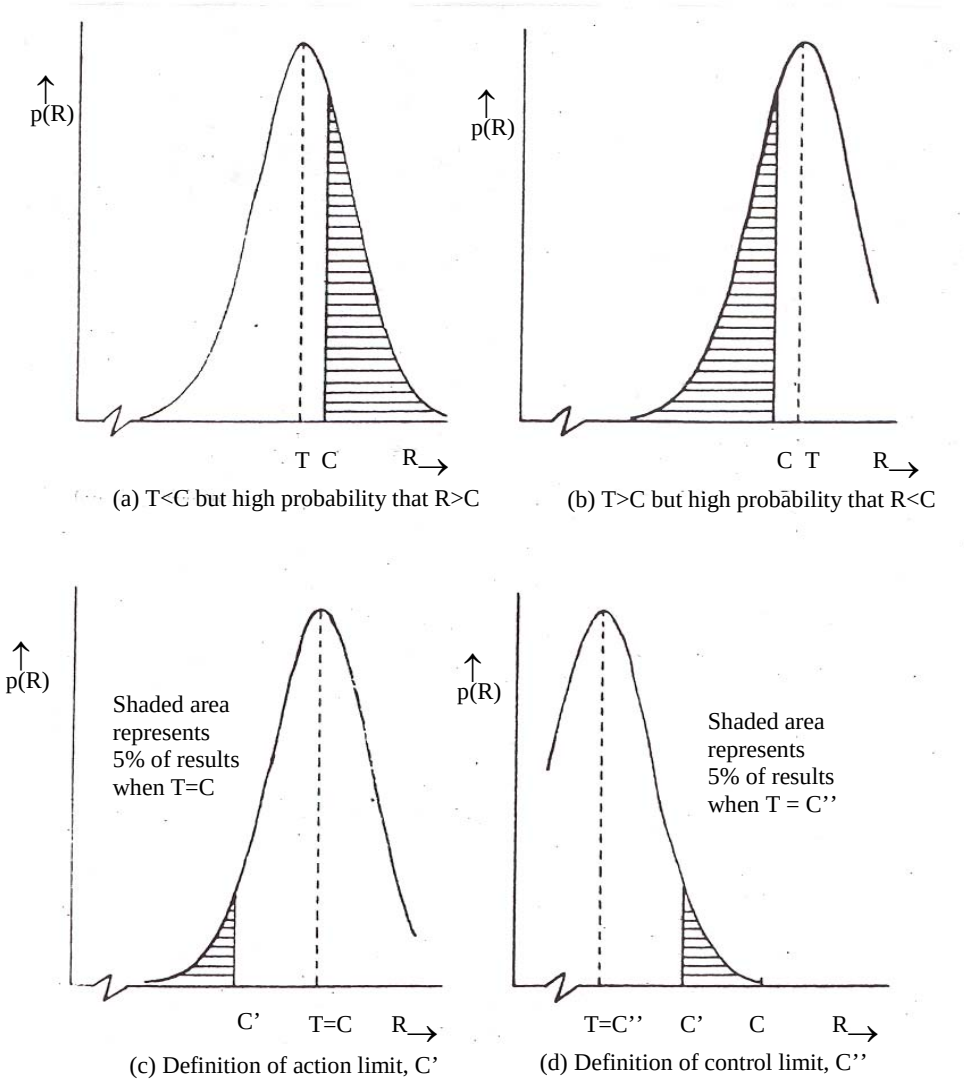

Figure 2(a)-(d). Effect of Random Errors on Decision-Making

Again, from the properties of the normal distribution, $C''=C'-1.64\sigma_{C''}$, where $\sigma_{C''}$ is the standard deviation of measurement results at the concentration C". It follows that $C''=C-1.64(\sigma_C+\sigma_{C''})$.

If it is assumed that σ is independent of the concentration of the parameter in the range between C" and C, the previous equation can be solved to give $\sigma=(C-C'')/3.28$.

Figure 2(e) combines the two curves presented in Figures 2(c) and 2(d) to show the relationships between the control and action limits.

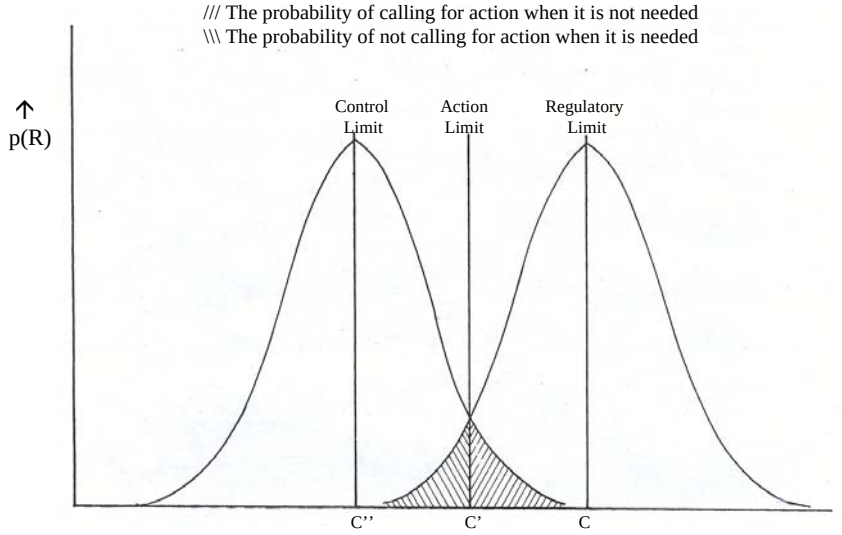

Figure 2(e). Statistical Approach to Decision-Making

Note that C' is the action limit or critical level for decision-making. Decisions are made at the action limit and not at the regulatory limit, in order to reduce Type I errors.

C" is called the control limit because in some environmental situations, such as the operation of a treatment plant or when it is possible to change the inputs of pollution to the environment, one can take measures to control the concentration below C". In other environmental situations such as cleanup of a hazardous waste site, there is no control of the concentration, but C" can be established in order to determine how many samples need to be taken to reduce the effect of Type II errors on decision-making.

The above considerations provide the basis for EPA's procedure for specifying tolerable limits on decision errors, as described in EPA documents (QA/G-4 and QA/G-4HW) and software (QA/G-4D). While the normal distribution curves in Figures 2(a) through 2(e) are not shown in these EPA documents, they provide the theoretical basis for the construction and use of the Decision Performance Curve and Decision Performance Goal Diagrams used by EPA for decision-making.

Figure 3 is an example of a Decision Performance Curve taken from EPA QA/G-4. This curve illustrates how the probability of deciding that the parameter exceeds the standard or regulatory level changes as the true value of the parameter changes. For an ideal decision performance curve where random error is considered to be negligible, the probability is zero until the standard or regulatory level is reached. But for a realistic decision performance curve representing a real-world situation with random error, the probability gradually increases and does not reach 100% until the standard or regulatory level is exceeded. In statistical terms, the realistic decision performance curve is a plot showing how β changes as the true value of the parameter changes. EPA refers to this as a power curve, although usually a power curve is a plot of $1-\beta$ against the true value.

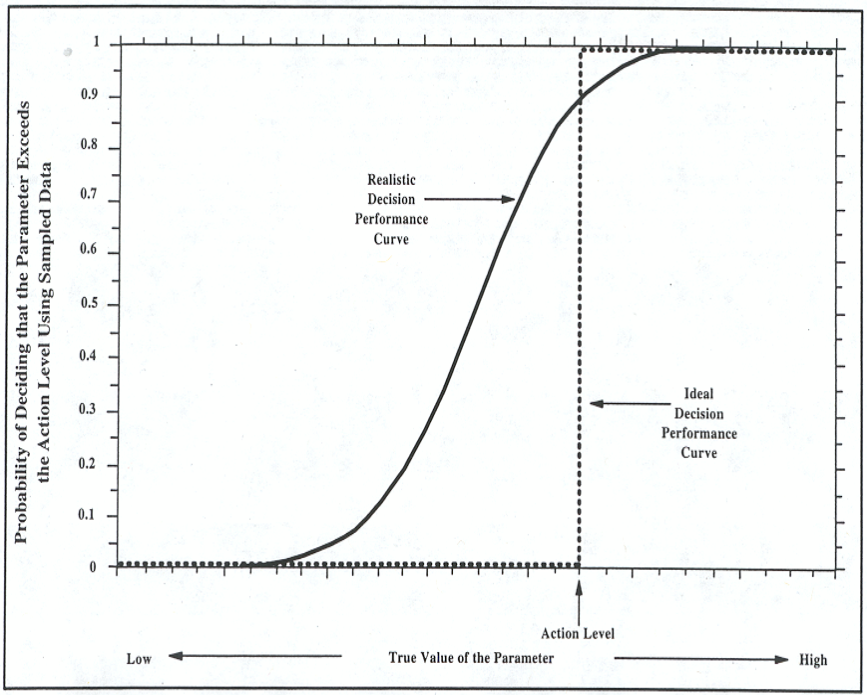

Figure 3. An Example of a Decision Performance Curve

In Figure 3 the action level is equal to the standard level being enforced. This conflicts with the statistical analysis, which showed that the action level must be less than the standard level being enforced in order to reduce the probability of a false positive error. EPA explains this by distinguishing between a theoretical decision rule during the planning stage and an operational decision rule used in the assessment stage. The theoretical decision rule assumes that you know the true value of the parameter, while the operational decision rule is used after you have obtained results for measurements made on the samples.

In the planning process, EPA QA/G-4 specifies that one construct a Decision Performance Goal Diagram (DPDG) which approximates a Decision Performance Curve, based on the choices you make for tolerable false acceptance decision rates and tolerable false rejection decision error rates.

The American Society of Testing and Materials (ASTM) publication ASTM D5792-95, *Standard Practices for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives*, uses an operational decision rule both in the planning and assessment stages. This is consistent with the statistical analysis presented above, and the action level is defined the same way during planning and implementation stages. Figure 4, taken from ASTM D5792-95, shows a Decision Performance Curve. In this case, $\alpha = 0.2$ and $\beta = 0.1$, and the regulatory threshold is equal to 1.0 mg/L. It illustrates that the operational action level corresponds to the concentration with a 0.5 probability of taking action, which is the mid-point of the decision performance curve.

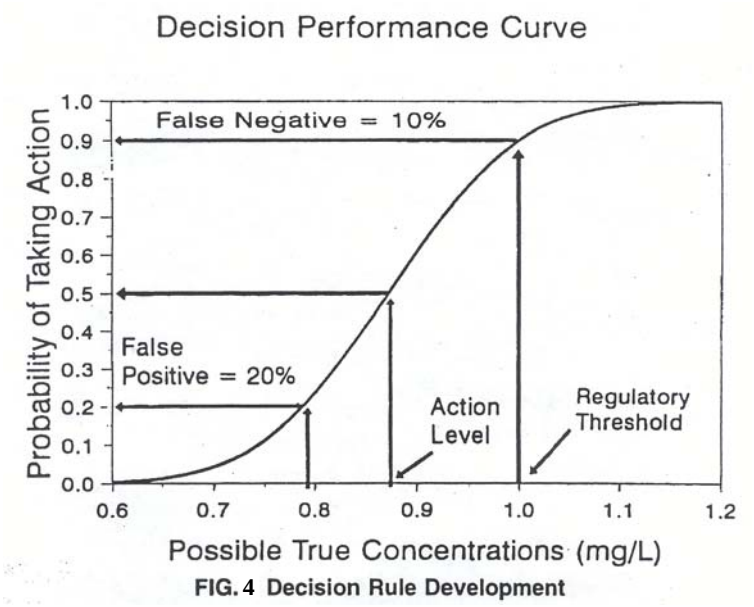

FIG. 4 Decision Rule Development

Appendix A of *Data Quality Objectives Process for Hazardous Waste Site Investigations* (EPA QA/G-4HW) presents a comparison of DQO Process Documents, which includes the EPA and ASTM DQO Processes already mentioned, as well as the U.S. Department of Energy *Streamlined Approach for Environmental Restoration* (SAFER) Process.

A priori decision-making occurs before the data are collected, during the planning stage. As explained above, when planning projects that involve decisions as to whether a standard has been exceeded, you must choose the desired probabilities of Type I and Type II errors for the data. You must also choose the minimum detectable difference (delta, δ). In Figure 2(e), this minimum detectable difference is the range between C" and C or 3.28σ. In the QA/G-4 document, EPA designates this range as the gray region. It helps to understand that the distributions illustrated in Figure 2(e) determine the gray region.

There are two ways of improving precision in order to reduce the minimum detectable difference or gray region:

1. Use more precise sampling and analysis procedures
2. Take replicate samples for analysis and use the mean result

The standard error of the mean is equal to $s/\sqrt{n}$, so the precision of a mean result as compared with an individual result is improved by a factor of $1/\sqrt{n}$. Taking replicate samples is a very practical way to improve precision for decision-making, and Decision Performance Goal Diagrams help you to decide how many samples must be taken to achieve the precision needed for decision-making.

The number of samples that must be analyzed is determined from the chosen values of α, β, and δ. These, along with the value for σ, will determine how many samples need to be included in each mean result. Ideally, the value assigned to σ will be based on an estimate from previous sample analyses at the site. If not, make a preliminary estimate using your best judgement. The bottom line is that you can choose the number of samples needed to ensure that, if the true value is equal to C", the probability of deciding incorrectly that the standard has been exceeded should be equal to β.

The formula for calculating the sample size, assuming simple random sampling, needed to meet the conditions specified for α, β, δ, and σ is given by:

$$n = \frac{\sigma^2 (z_{1-\alpha} + z_{1-\beta})}{\delta^2} + \frac{z_{1-\alpha}^2}{2}$$

where z_p=the p^{th} percentile of the standard normal distribution.

When $\alpha=\beta=0.05$, this equation can be solved for the minimum detectable difference, δ,:

$$\delta = \frac{3.28\sigma}{\sqrt{n}}$$

Thus, for the example given in Figure 2(e), the value of n can be calculated by solving this equation for n, i.e., $n \cong 10.8(\sigma/\delta)^2$. This aspect of choosing n so that a test is capable of detecting a difference when the population mean differs from a fixed value (e.g., regulatory limit) by a specified amount is known as “ensuring adequate *power* of the test.”

EPA has provided software that will calculate n for the case described above, as well as for other sampling designs. The latest version of that software, Decision Error Feasibility Trials (DEFT), is available at the web site listed in Appendix J

The U.S. Department of Energy also provides software called Visual Sample Plan (VSP) which provides statistical solutions to sampling design and answers two important questions in sample planning: (1) How many samples are needed? and (2) Where should the samples be taken? VSP is available at the web site listed in Appendix J.

A posteriori decision-making occurs after the data are collected, during the data quality assessment stage, and is based solely on the probability of Type I error, α. The action level (critical level in statistical terminology) should be near the concentration C' established during the planning process. However, the actual decision level will be determined by performing a t-test. The t-test is done to test the null hypothesis that the mean is equal to or greater than the standard or regulatory threshold (C) against the alternative hypothesis that the mean is less than C.

The t-statistic is calculated as follows:

$$t_{calc} = \frac{\left|\bar{x} - E\right|}{s / \sqrt{n}}$$

where E = the expected or standard value (C)
s = the estimated standard deviation of a single result
and n results have been used in calculating the mean

The value of t_{calc} is compared with a value of t found in a table (t_{tabl}) based on the number of degrees of freedom used in estimating s and the value of α chosen previously. For this test, one rejects the null hypothesis if t_{calc} is less than t_{tabl}. Note that this is a one-sided test in which the mean being tested is less than the expected or standard value.

Effect of Bias

As a general rule, it is preferable, and sometimes essential, to ensure that bias is negligible. EPA QA/G-4 assumes negligible bias in specifying tolerable limits on decision errors. Unfortunately, it is often the case that significant bias is present in sampling and analysis.

Unrepresentative sampling contributes to biased results; therefore, it is important to have a good sampling plan and ensure that operational implementation of the plan gets representative samples.

Results obtained from the use of many analytical methods, especially those involving extraction of organic compounds from environmental matrices, exhibit negative bias caused by differences in procedures for calibration and sample analyses. Bias may also be caused by interference or failure to allow for blank correction. The project manager should be aware of the bias inherent in the use of some methods, and coordinate with the laboratory to choose methods that are capable of meeting the targets for bias established in the MQOs.

Since there are several possible causes for bias, and bias can vary with concentration as well as from sample to sample and from time to time, it is not generally possible to eliminate bias by measuring it and making a correction to the result for each sample.

When random error is negligible, the only generally effective approach that can be used to account for bias is to change the action level to allow for it. For example, if the standard is C and negative bias is present, one could control at $C-\beta_c$, where β_c is the bias present at concentration C.

When both bias and random errors are present, there is no simple and general approach that overcomes the problems involved in the interpretation of results. It is usually possible to obtain an estimate of the random error of a particular result, but much more difficult to estimate the bias. Therefore, emphasis should be placed on ensuring that the magnitude of bias is as small as possible. Finally, one can shift the action level to a lower or higher value, depending on whether

the estimated bias is positive or negative. As already stated, when considering bias alone, one changes the control to C-β_c. If you consider both bias and random error, one would control random errors below C-β_c-3.29σ, where σ is the standard deviation of analytical results and is assumed to be independent of the concentration of the analyte.

Paired-Comparison Test

The paired-comparison test is a very useful and simple statistical test that can be applied to answer questions that frequently arise in assessing data from environmental projects. Examples include the comparison of pairs of upstream and downstream results over time, the comparison of results before and after cleanup, and the comparison of pairs of results for samples analyzed by two different methods. The paired-comparison test is a variation of the basic t-test, which is used to test whether there is a statistically significant difference at a given probability level between the means of two independent sets of results.

The paired-comparison test is an application of the formula given above, to compare two pairs of results, where the expected difference between each of the pairs of results is zero.

$$\text{i.e., } t = \frac{\bar{x} - 0}{s / \sqrt{n}}$$

The following is an example of the paired comparison test to compare results for samples analyzed using two different methods of analysis and to determine if there is a statistically significant difference between the results.

Original Results				
Method A	Method B	Difference B-A	Coded difference, D	D^2
2.5	2.8	0.3	3	9
4.2	4.1	-0.1	-1	1
7.3	8.6	1.3	12	169
1.4	1.7	0.3	3	9
3.6	3.9	0.3	3	9
5.9	6.6	0.7	7	49
4.5	4.5	0.0	0	0
3.2	4.0	0.8	8	64
			$\Sigma D=36$	$\Sigma D^2=310$

$(\Sigma D)^2/n = 1296/8 = 162$

$$s = \sqrt{\frac{\sum D^2 - \frac{(\sum D)^2}{n}}{n-1}} = \sqrt{((310\text{-}162)/7)} = 4.598 \text{ with 7 degrees of freedom}$$

$t = (\,|\,(\Sigma D)/n\text{-}0\,|\,)/(s/\sqrt{n}) = (4.5\sqrt{8})/4.598 = 2.77$ with 7 degrees of freedom.

For a significance level, α=0.05, the tabulated value corresponding to t_α for 7 degrees of freedom is 2.36. The observed value, 2.77, is greater than the tabulated value; the difference between Methods A and B is therefore statistically significant.

References

"Guidance for the Data Quality Objectives Process", EPA QA/G-4, August 2000.

"Data Quality Objectives Process for Hazardous Waste Site Investigations", EPA QA/G-4HW, January 2000.

"The Chemical Analysis of Water", by D.T.E. Hunt & A.L. Wilson, The Royal Society of Chemistry, 2nd edition, 1986.

"Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives", ASTM Designation: D5792-95, American Society for Testing and Materials, January 1996.

"A Manual on Analytical Quality Control for the Water Industry", by R.V. Cheeseman and A.L. Wilson (Revised by M.J. Gardner), NS 30, Water Research Centre, England, June 1989.

Module 7, "Streamlined Approach for Environmental Restoration (SAFER)" in *Remedial Investigation/Feasibility Study (RI/FS) process, Elements and Technical Guidance*, U.S. Department of Energy (DOE), EH 94007658, December 1993.

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Appendix F

Approach to Analytical Quality Control of the Water Research Centre

The recommended approach to analytical quality control (AQC) is summarized in the sequence of activities below, which includes a brief statement of the main purpose of each activity. The sequence is followed for each parameter, and no stage should be started until the preceding stage has been completed. The aim is to ensure proper and progressive control of different types of error so that if problems arise, their source may be more readily identified and eliminated. This approach does not lead to rapid progress, but experience has shown that only this logical sequence for the assessment and control of errors is likely to lead to satisfactory accuracy in participating laboratories.

It has been successfully applied in England and used as the basis for AQC by the United Nations Environmental Program for Global Water Quality Monitoring. Analytical objectives are stated in terms of precision, bias, and the lowest concentration of interest. The Water Research Centre refers to "targets" for precision and bias, which are comparable to the measurement quality objectives (MQOs) described in this document.

The following general approach is used in step 2 for specifying the maximum tolerable random and systematic errors of individual analytical results:

- "The systematic error of individual analytical results should not exceed c concentration units or p% of the result, whichever is the greater."
- "The random error of individual analytical results should not exceed c concentration units or p% of the result, whichever is the greater."

These two statements are equivalent to "The total error of individual analytical results should not exceed 2c concentration units or 2p% of the result, whichever is the greater."

By stating these targets in statistical terms, one can use analysis of variance (ANOVAR) to determine whether the targets have been met at a chosen statistical level of confidence. This enables one to confirm that analytical MQOs have been met before routine sampling begins.

Additional information on this approach to AQC can be found in the following:

"A Manual on Analytical Quality Control for the Water Industry", by R.V. Cheeseman and A.L. Wilson (Revised by M.J. Gardner, June 1989), Publication NS 30, Water Research Center plc, England.

"The Chemical Analysis of Water", 2nd Edition, 1986, by D.T.E. Hunt and A.L. Wilson, The Royal Society of Chemistry.

Sequence of Activities for Analytical Quality Control

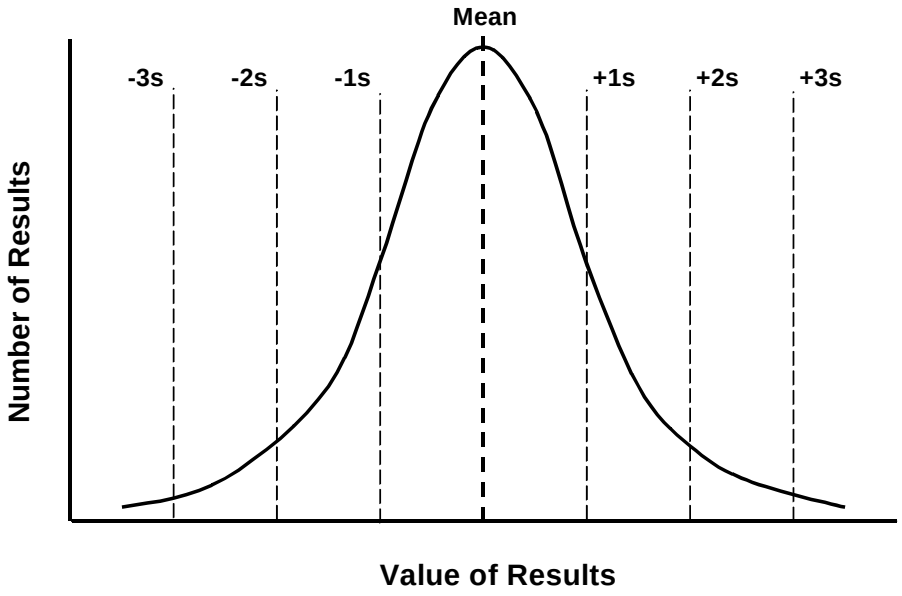
Activity	Purpose
1. Establish working group	To plan and coordinate subsequent activity.
2. Define analytical objectives	To ensure clear specification of analytical requirements.
3. Choose analytical methods/ systems*	To select methods/systems capable of the required accuracy.
4. Ensure unambiguous description of methods	To ensure that the chosen methods are followed properly.
5. Estimate within-laboratory precision and spiking recovery	To ensure that each laboratory achieves adequate precision and to check certain sources of bias.
6. Ensure accuracy of standard solutions. Preliminary check on interlaboratory bias	To eliminate this source of bias in each laboratory and to prepare full, more detailed bias checks.
7. Set-up quality-control charts	To maintain a continuing check on analytical performance in each laboratory.
8. Undertake tests of interlaboratory checks	To ensure that each laboratory achieves adequately small errors.
9. Maintain accuracy using control charts and regular follow-up interlaboratory tests	To ensure long-term control of the accuracy and comparability analytical results.

* The analytical method is the set of written instructions followed by the analyst. The analytical system includes all aspects of producing results (e.g., method, equipment, analyst, laboratory environment).

Appendix G

Statistical Calculations Related to Data Quality

The results obtained from the Quality Control (QC) procedures described in Element 10 can provide an indication, and even a quantitative estimate, of the error associated with measurement data. If a physical or chemical measurement is repeated many times using a sufficiently sensitive procedure, the probability distribution of the results will resemble the familiar bell-shaped curve shown here.



The curve, which represents a normal distribution, is characterized by its mean value, which defines the center of the distribution, and by its standard deviation, *s*, which describes the width or dispersion of the distribution. The difference between the population mean and the true value is the bias in the results and the standard deviation is the variability due to random error.

Here are some equations you can use to evaluate the quality of measurement data.

Precision

Precision is estimated as the standard deviation of the results of *n* replicate measurements by

$$s = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2/n}{n-1}} \qquad (1)$$

where x_i is the *i*th result in the set of *n* results. This function is available on most scientific calculators.

For duplicate results, Equation 1 becomes

$$s = \frac{|D|}{\sqrt{2}} \qquad (2)$$

where D is the difference between the two results.

If more than one estimate of the standard deviation of a population is available, a pooled estimate, s_p, may be calculated from

$$s_p = \sqrt{\frac{\sum \nu_i s_i^2}{\sum \nu_i}} \qquad (3)$$

where $\nu_i = n_i - 1$, the number of degrees of freedom associated with the estimate of s_i.

For m pairs of duplicate results, Equation 3 reduces to

$$s_p = \sqrt{\frac{\sum D^2}{2m}} \qquad (4)$$

The estimate of standard deviation improves as the number of degrees of freedom increases. For a better estimate of s, plan to collect and/or analyze more replicates or more pairs of duplicates.

The pooling equations assume that the standard deviations are all from the same population of results. Since the standard deviation varies with the magnitude of the results, the pooling equations should be used only for results of approximately the same magnitude. As a rule of thumb, use results that are within one order of magnitude for pooling standard deviations. If your study involves a wide range of results, it might be necessary to obtain separate estimates of standard deviation for several ranges of concentration.

Precision is often reported as the Relative Standard Deviation (RSD) of the results of replicate measurements, which is calculated as a percentage of the mean by

$$RSD = \frac{s}{\bar{x}} \cdot 100 \qquad (5)$$

where $\bar{x}$ is the mean of the replicate measurements.

Sometimes the precision of differences between duplicate results is expressed as the Relative Percent Difference (RPD), which is calculated as

$$RPD = \left(\frac{|R_1 - R_2|}{R_1 + R_2} \right) \times 200$$

where R_1=Result for the first measurement
and R_2=Result for the second measurement

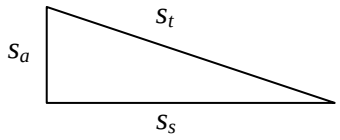
The total precision of results can be estimated from the results of replicate field measurements or replicate samples. Analytical precision can be estimated from the results of replicate analyses of samples or check standards.

The total standard deviation estimated from the analysis of replicate samples, s_t, is given by

$$s_t^2 = s_s^2 + s_a^2 \qquad (6)$$

where s_s = the standard deviation due to sampling
and s_a = the standard deviation due to analysis

In this equation the variances, s^2, are additive rather than the standard deviations. This is analogous to the Pythagorean theorem for right triangles, where the lengths of the sides of the triangles are given by s_a, s_s and s_t as shown below



Rearranging equation (6) gives an estimate of the variability due to sampling,

$$s_s = \sqrt{s_t^2 - s_a^2} \qquad (7)$$

For example, suppose that, for a set of samples, the results of analysis of field replicates yield an estimate of total standard deviation of 0.50 for a particular parameter. Suppose further that pooling the results for analytical duplicates yields an estimate of the standard deviation of 0.20. Equation 7 provides an estimate of standard deviation due to sampling of 0.46, which means that the sampling procedures are responsible for most of the uncertainty in the results.

To improve the total precision of these results, you will need to find a way to reduce the variability introduced by the sampling procedures because improving the analytical precision has little effect on total precision. In this case, reducing the analytical standard deviation by half to 0.10 reduces the total standard deviation by only 6% to 0.47.

If you plan to base a decision on a mean of several sample results, you can estimate the confidence interval on that mean by

$$CI = \bar{x} \pm t_{(1-\alpha,\nu)} s_x/\sqrt{n} \qquad (8)$$

where *t* is the appropriate value of Student's-t statistic for the desired level of confidence $(1 - \alpha)$ and the number of degrees of freedom (ν).

If the standard deviation has been estimated from a reasonable number of sample results (at least 10), confidence intervals can be assigned to individual results. The confidence interval for a result, *x*, is given by

$$CI = x \pm t_{(1-\alpha,\nu)}s_x \qquad (9)$$

Suppose that the mean of the results of 10 replicate determinations is 11.3 and the standard deviation is 1.0. To determine the 95% confidence interval on the mean, look up the value of the 5% point (double-sided test) of the Student's t-statistic for 9 degrees of freedom, which happens to be 2.26. Using Equation 8,

$$95\% \text{ CI on the Mean} = 11.3 \pm 2.26(1.0)/\sqrt{10}$$

$$= 11.3 \pm 0.7$$

Thus there is a 95% chance that the actual value of the mean lies between these values, assuming no bias in the results.

On the other hand, suppose you need to estimate the confidence interval on just one of those 10 results, say $x = 12.4$. Then Equation 9 gives

$$95\% \text{ CI on } x = 12.4 \pm 2.26(1.0)$$

$$= 12.4 \pm 2.26$$

$$= 10.1 - 14.7$$

and there is a 95% chance that the actual value for that sample lies between these values.

This example demonstrates that the mean of several results gives a much more precise estimate of the population mean than can be obtained with any single result, a consequence of the fact that the standard error of the mean is equal to $s/\sqrt{n}$.

Precision must be considered when comparing results to other data or to fixed limits. For example, if the confidence interval for a result includes the regulatory limit, then no decision can be made as to whether the limit was exceeded, and an objective of the study may not be achieved. Also, if the confidence intervals for the results from two locations or time periods overlap, then the two sets of results are not statistically different at the probability level selected for the comparison.

If replicate measurements are not greater than the reporting limit, precision cannot be estimated for that parameter. Thus, it is important to select samples to be analyzed in replicate which are likely to give results greater than the reporting limit. There is no need to randomly select measurements or samples for replication. The more information and professional judgement you can bring to the selection process, the more likely you are to obtain useful information from the results.

Bias

The determination of bias due to sampling procedures requires special studies designed to examine the various sources of error. Such studies have led to the recommended procedures for sample collection, preservation, etc. currently in use. Careful adherence to the procedures selected for the project should maintain bias within acceptable limits.

Two potential sources of systematic error (bias) in a measurement are calibration and interferences due to the sample matrix. The results for analyses of check standards can be used to estimate bias due to calibration error. The results for analyses of matrix spikes can be used to detect interference effects due to the sample matrix.

An estimate of bias due to calibration is given by

$$B(\%) = \frac{\bar{x} - T}{T} \cdot 100 \qquad (10)$$

where $\bar{x}$ is the mean of the results of (at least 10) replicate analyses of the check standard, and T is the true concentration. If the confidence interval on the mean includes T, the difference is probably due to random error rather than bias. The analyst should monitor check standard results and recalibrate the instrument when the difference exceeds the laboratory's control limits.

For matrix spikes, the percent recovery (%R) is given by

$$\%R = \frac{x_s - x}{C_s} \cdot 100 \qquad (11)$$

where x_s is the result for the matrix spike, x is the result for the unspiked sample, and C_s is the concentration of the spike added to the sample.

Bias is judged to be present when the %R falls outside the control limits established by the laboratory based on historical data. When this occurs, the analytical procedure should be modified to eliminate the interference effects if possible.

Since the %R is a function of the difference between two results, its uncertainty is relatively large, and the power of the spike recovery test to detect bias is therefore low. For this reason, correction of the sample results based on matrix spike recovery is not recommended.

If QC results exceed their criteria and no corrective action is taken by the laboratory, the sample results should be qualified as estimated or unusable. If data verification and validation reveal significant bias indicated by QC results, the project manager may need to conclude that the data cannot be used or that they should be qualified for the purpose of the project.

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Appendix H

Examples of Tables

Measurement Quality Objectives*

Example of completed measurement quality objectives table for parameters in water:

Parameter	Check standard (LCS)	Duplicate samples	Matrix spikes	Matrix spike duplicates	Surrogate standards	Lowest concentrations of interest
	% recovery limits	RPD	% recovery limits	RPD	% recovery limits	units of concentration
Alkalinity	80-120	20	NA	N/A	N/A	5 mg/L
Orthophosphate	80-120	20	75-125	20	N/A	5 µg/L
Cadmium	85-115	20	75-125	20	N/A	10 µg/L
BNA	40-150	50	40-150	40	10-150**	5 µg/L
Organochlorine Pesticides (ECD)	30-150	50	30-150	50	30-150	10 µg/L
pH***	±0.1 pH units	±0.05 pH units	N/A	N/A	N/A	N/A

RPD - relative percent difference

BNA - base/neutrals and acids

* - This table is constructed with the same units used to report results for laboratory QC analyses. Information on the default QC sample types and QC limits can be obtained from the laboratory that will perform the analyses. An exception is pH which is analyzed in the field.

** - Surrogate recoveries are compound specific.

******* - pH is measured in the field, and accuracy is ensured by calibrating the instrument before and after use.

Sample Containers, Preservation, and Holding Times

Example of completed table

Parameter	Matrix	Minimum quantity required	Container	Preservative	Holding time
Alkalinity	Surface water	500 mL	500 mL wide-mouth polyethylene	Cool to 4° C	14 days
Orthophosphate	Surface water	125 mL	125 mL amber wide-mouth polyethylene	Cool to 4° C	48 hours
Cadmium	Marine water	500 mL	1 L HDPE with Teflon®-lined lid	pH < 2, Cool to 4° C	6 months
BNA	Ground water	1 gallon	1 gal. glass with Teflon®-lined lid	Cool to 4° C	7 days
Organochlorine Pesticides	Surface water	1 gallon	1 gal. glass with Teflon®-lined lid	Cool to 4° C	7 days

BNA – base/neutrals and acids
HDPE – high-density polyethylene

The information required for this table is available in the following publications:

- Manchester Environmental Laboratory, *Lab Users Manual* (Ecology, 2003b)
- 40 CFR 136.3, Table II
- SW-846 Methods, Section 6.0
- EPA/600/R-93/100, *Methods for the Determination of Inorganic Substances in Environmental Samples*, August 1993

Measurement Methods

Example of completed table

Analyte	Sample matrix	Samples [number/ arrival date]	Expected range of results	Reporting limit	Sample preparation method	Analytical method
Alkalinity	Surface water	20 on 11/22/00	50 - 100 mg/L	5 mg/L	N/A	SM 2320 Titration
Orthophosphate	Surface water	20 week of 7/5/00	0 - 0.05 mg/L	0.003 mg/L	N/A	EPA 365.3 Colorimetric Ascorbic Acid
Cadmium	Marine water	8 first week of August + 8 two weeks later	10 - 100 µg/L	5 µg/L	Total Acid Digestion	EPA 200.7 ICP/AES
BNAs	Ground water	10 last week of June	0 - 200 µg/L	1 - 5 µg/L	L-L Extraction	EPA 8260 GC/MS
Organochlorine Pesticides	Surface water	10 last week of June	0 - 100 µg/L	0.01 – 0.1 µg/L	SPE	EPA 8081

BNA - base/neutrals and acids

QC Samples, Types, and Frequency

Example of completed QC procedures table

Parameter	Field		Laboratory			
	Blanks	Replicates	Check standards	Method blanks	Analytical duplicates	Matrix spikes
pH	N/A	1/day	1/day in field	N/A	N/A	N/A
Orthophosphate	1/site	1/site	1/batch	1/batch	1/batch	None
Cadmium in water	1/day	1/10 samples	1/batch	1/batch	1/batch	1/batch
Cadmium in sediment	1 background	1/10 samples	1/batch	1/batch	1/batch	1/batch
BNA	1 transfer/day	1/day	1/batch	1/batch	1/batch	1/batch
Fecal coliform bacteria	N/A	1/20 samples	N/A	2/batch	N/A	N/A

BNA - base/neutrals and acids

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Appendix I

Calibration

Calibration relates the response of the measurement system to the property of the sample being measured. It is an essential component of the measurement system itself, necessary before any quality control procedures can be performed. In general, calibration standards should be analyzed by the same procedure used to analyze the samples. Failure to do so can introduce bias in sample results. This principle is often not followed, and calibration bias is found in many methods, particularly for organics parameters. It shows up as low percent recoveries for check standards and surrogates.

In order to use the same calibration procedure to analyze samples of different matrices, the calibration procedures may be different from those used to analyze the samples.

For most analytical procedures, calibration is required each day, shift, or sample batch. This is called within-batch calibration. For within-batch calibration, a blank and four standards are recommended for most systems.

Some measurement systems (e.g., UV-VIS Spectrophotometers) are sufficiently stable that a calibration curve can be used for a long period of time. This is called fixed calibration. It is recommended that fixed calibrations be based on a blank and at least seven standards. The fixed calibration is not repeated until the results for the check standards indicate the need to do so.

Most measurement systems are calibrated with external standards. The response of one or more standards is recorded and used to evaluate the response of the samples.

Internal standards are used in some analytical methods such as gas chromatography/mass spectrometry (GC/MS). One or more internal standards are added to each sample or sample extract. In GC-MS the internal standards are isotopically-labeled compounds. Calibration and sample quantification are based on the ratio of the response of the compound of interest to that of the associated internal standard.

The Method of Standard Additions (MSA) is used in some methods, such as metals analysis by Graphite Furnace Atomic Absorption Spectroscopy (GFAA) to correct for bias due to interference. The interference effects must be proportional to the concentration of the target analyte for MSA to provide accurate results. Standards at several concentrations are added to aliquots of the sample, and the resulting calibration curve is used for quantitation.

Finally, sample responses must fall within the range of the calibration curve. This is why it is important to provide the lab with any available information on the expected levels of contaminants in your samples.

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Appendix J

Web Sites

Washington State Department of Ecology http://www.ecy.wa.gov

Environmental Assessment Program Publications http://www.ecy.wa.gov/biblio/eap.html

List of Accredited Laboratories, non-Drinking Water
http://www.ecy.wa.gov/programs/eap/labs/labs_pl.pdf

List of Accredited Laboratories, Drinking Water
http://www.ecy.wa.gov/programs/eap/labs/srchmain.htm

Manchester Lab Methods http://www.ecy.wa.gov/programs/eap/manchester/melmeth.htm

Manchester Lab Users Manual*
http://aww.ecolgy/programs/eap/Documents/labmanual.pdf

Guidelines for Technical Document Review*
http://aww.ecology/programs/eap/Policies/04-01%20Policy-Tech%20Guidance.pdf

*Available only to Ecology staff on the agency Intranet

American Society for Testing and Materials (ASTM) http://www.astm.org

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Federal Remediation Technologies Roundtable http://www.frtr.gov

Field Sampling and Analytical Technologies Matrix http://www.frtr.gov/site

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Hanford Site http://www.hanford.gov/hanford.cfm

Data Quality Objectives http://www.hanford.gov/dqo

National Institute of Standards and Technology (NIST) http://ts.nist.gov

Standard Reference Materials (SRMs) http://ts.nist.gov/ts/htdocs/230/232/232.htm

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Pacific Northwest Laboratory (Battelle) http://www.pnl.gov

Statistics http://www.pnl.gov/Statistics

Data Quality Objectives http://dqo.pnl.gov/

Visual Sample Plan http://dqo.pnl.gov/vsp/

Puget Sound Action Team http://www.psat.wa.gov

PSEP Protocols http://www.psat.wa.gov/Publications/protocols/protocol.html

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Synectics

Analytical Methods and other Technical Documents for Environmental Professionals
http://synectics.net/resources

U.S. Environmental Protection Agency http://www.epa.gov/

Office of Environmental Information http://www.epa.gov/oei

Quality Staff http://www.epa.gov/quality/

Quality System Documents http://www.epa.gov/quality/qa_docs.html

Index to EPA Test Methods http://www.epa.gov/epa home/index
(Includes links to sources of EPA methods)

Volunteer Stream Monitoring: A Methods Manual
http://www.epa.gov/owow/monitoring/volunteer/stream

The Triad Approach http://www.epa.gov/tio/triad/index.htm

Biological Assessment of Streams and Rivers http://www.epa.gov/bioindicators/html/qapp.html

Dynamic Field Activities http://www.epa.gov/superfund/programs/dfa/decsupp.htm

Systematic Planning http://www.epa.gov/superfund/programs/dfa/systplan.htm

Field Analytical Methods http://www.epa.gov/superfund/programs/dfa/fldmeth.htm

Decision Support Software http://www.epa.gov/superfund/programs/dfa/decsupp.htm